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# Use and Production of Iron Salts for Phosphorus Removal

## Research Report No. 5



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1973  
MOE

Research Program for the Abatement of Municipal Pollution  
under Provisions of the Canada-Ontario Agreement  
on Great Lakes Water Quality

RESEARCH REPORT NO. 5  
USE AND PRODUCTION OF IRON SALTS FOR PHOSPHORUS REMOVAL

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Use and production of iron salts  
for phosphorus removal / Scott,  
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USE AND PRODUCTION OF IRON SALTS  
FOR PHOSPHORUS REMOVAL

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RESEARCH PROGRAM FOR THE ABATEMENT  
OF MUNICIPAL POLLUTION WITHIN THE  
PROVISIONS OF THE CANADA-ONTARIO  
AGREEMENT ON GREAT LAKES WATER QUALITY

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### Abstract

The use of iron salts for the precipitation of phosphorus from waste waters is discussed. Evidence is reviewed which suggests that ferrous and ferric salts behave in an equivalent manner because of the rapid oxidation of the former in neutral solutions. The market for phosphorus removal chemicals in Ontario is estimated, and from this, the probable pattern of growth of the market for soluble iron salts is predicted.

Because of the low cost and ease with which iron salts may be manufactured locally from waste iron-containing materials and from sulphuric acid, it is shown that the use of imported iron salts would represent a loss of economic benefits to the province of Ontario. A summary is given of the nature, source, composition and reactivity with dilute sulphuric acid of major iron-containing waste materials available in Ontario. The costs of manufacturing ferrous or ferric sulphate at different production capacities from a number of these materials have been estimated. Treatment costs for phosphorus removal using iron sulphate could be as low as \$10-\$20 per million gallons. For almost all combinations of circumstances, the use of locally manufactured iron sulphates will be competitive with or cheaper than either alum or imported salts, and in most cases will be significantly cheaper.

## Résumé

Le présent ouvrage traite de l'utilisation de sels de fer pour précipiter le phosphorus des eaux usées. Il revoit les faits qui portent à croire que les sels ferreux et ferriques se comportent de la même manière en raison de l'oxydation rapide des premiers dans les solutions neutres. On y donne une estimation du marché qui existe en Ontario pour les produits chimiques servant à la déphosphoration et, d'après cette estimation, on prévoit la croissance probable du marché de sels de fer solubles.

Etant donné le faible coût et la facilité avec lesquels on peut produire localement des sels de fer à partir de ferraille et d'acide sulfurique, il est démontré que le recours aux sels de fer importés serait au désavantage économique de la province d'Ontario. L'ouvrage comprend un résumé de la nature, de la source, de la composition et de la réactivité à l'acide sulfurique diluée des principaux déchets à teneur en fer disponibles en Ontario. Les coûts de fabrication du sulfate ferreux ou ferrique, à diverses capacités de production, ont été estimés en rapport avec un certain nombre de ces matériaux. La déphosphoration à l'aide de sulfate de fer pourrait ne coûter que de \$10 à \$20 le million de gallons. Dans presque toutes les circonstances possibles, il serait aussi avantageux sinon plus d'utiliser du sulfate de fer produit localement que d'avoir recours à de l'alun ou des sels importés; et dans la plupart des cas cela serait beaucoup plus économique.

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## CONCLUSIONS

1. In treatment plants having adequate aeration capacity, either ferrous or ferric salts are equally effective for phosphorus removal.
2. Because of lack of adequate aeration, jar tests using ferrous salts will give phosphorus removal levels which may be poorer than plant results.
3. The market for soluble iron salts for phosphorus removal will grow to about 15000 tons/year of soluble iron by 1980. Within a radius of 100 miles of Toronto this market will be about 10000 tons/year of soluble iron by 1980.
4. A total of about 1600 tons of iron per year is available in various Ontario locations as ferrous sulphate heptahydrate crystals. A further 800 tons per year is available as acidic ferrous sulphate solution (pickle liquor). This material is very cheap, and frequently represents a disposal problem for the producer.
5. Waste products containing iron are available, mainly in the Toronto-Hamilton area, in quantities considerably in excess of the requirements for iron salts. On the basis of tests of their rate of dissolution in dilute acid, several of these materials can be used for the manufacture of iron salts.
6. Estimates of manufacturing costs for ferrous or ferric sulphate solutions from commercial sulphuric acid and waste iron-containing materials suggest that this is potentially the cheapest chemical for phosphorus removal from waste waters for larger treatment plants. Treatment costs as low as \$10-\$20 per million gallons may be possible.
7. The cheapest source of iron salts for smaller plants is likely to be by-product ferrous sulphate or pickle liquors.
8. Iron salts are waste products in the United States, but importation of iron salts for use in phosphorus removal processes represents a direct economic loss to the economy of the province of Ontario, which has a glut of raw materials from which these salts can be made equally cheaply.



## RECOMMENDATIONS

1. Importation of iron salts for use as phosphorus removal chemicals should be strongly discouraged, because of the significant net economic costs that would result for the provincial economy.
2. The use of iron salts as phosphorus removal chemicals should be encouraged because of the significant potential savings compared to the use of other chemicals or imported salts.
3. The use of waste iron containing materials and waste acids to manufacture iron salts should be encouraged as an aid in alleviating some waste disposal problems of Ontario industries, and because of the additional savings in wastewater treatment costs which appear to be possible.
4. Smaller treatment plants should be encouraged to make use of by-product ferrous sulphate heptahydrate, or of pickle liquors, from metal fabricating operations. This can represent a saving in phosphorus removal costs, and simultaneously a solution to a locally troublesome industrial disposal problem. It should be noted that pickle liquor treatability studies have been carried out in Ontario (e.g., Dunnville and Chatham).

## USE AND PRODUCTION OF IRON SALTS FOR PHOSPHORUS REMOVAL

### INTRODUCTION

It is now recognized that the removal of phosphorus from waste waters in treatment plants can be carried out successfully at reasonable cost through the use of one of three treating chemicals - lime, alum or iron salts. Additions of lime or alum were the first to be used, probably for historic reasons, and their efficacy for phosphorus removal was demonstrated in both laboratory and field tests before iron salts had even been properly evaluated in the laboratory. However, in the last three years, the behaviour of iron salts as precipitants and settling agents has become better understood, and, in particular, the value of iron salts for phosphorus removal has been tested more adequately. Additional difficulties in assessing the effectiveness of iron salts for this purpose were caused by the fact that, in contrast to alum or lime, the iron can be added in either the di- or tri-valent state, and that several salts are available or could readily be made available in the required quantities.

Each treatment plant may have specific problems with the waste which must be treated, and because of these individual characteristics, it is difficult to say a priori that there is one best treatment for phosphorus removal. However, results of plant tests carried out in the United States in the last two to three years, (Leary et al (1972)), indicate that, for normal sewage, treatment with iron salts at low dosage rates gives very satisfactory results. Plant tests carried out in Ontario in the past, as well as tests presently being conducted, appear to confirm these conclusions. These results, and the potential ease of manufacture or supply of iron salts at a low cost, indicate that there may be a distinct economic advantage in the use of iron salts for phosphorus removal in a majority of treatment plants.

This report is part of the Canada-Ontario Agreement Project on the Availability and Quality of Waste Products for Phosphorus Removal.

## OBJECTIVES

The present study has as its principal objective an assessment of the supply and probable cost of iron salts for use as phosphorus removal chemicals in waste water treatment. Inasmuch as many industrial waste products are available which contain significant quantities of iron, an assessment of the location, availability and basic cost of these materials would be desirable. The suitability of these waste products for manufacture of iron salts, and the nature and purity of the resulting soluble product should be determined by laboratory testing, at least for those wastes likely to be of commercial value. The probable market pattern for iron salts for phosphorus removal must be estimated, and from these data, together with data from manufacturers and from the laboratory tests, the probable production costs of iron salts, and their probable cost to a treatment plant, can be determined.

Finally, some comparison of costs must be made between iron salts manufactured from waste materials and other commercially available chemicals presently used in phosphorus removal processes.

## CHARACTERISTICS OF IRON SALTS IN PHOSPHORUS REMOVAL

There are probably only four iron salts which can be considered to be presently available, or which could be made available, at prices competitive with lime or alum and in the tonnages required for phosphorus removal. These salts are ferrous chloride or sulphate and ferric chloride or sulphate. There has been some question in the past as to whether ferrous or ferric salts are more effective in phosphorus removal and subsequent sludge settling and handling. Conventional jar tests usually gave results showing a clearly better performance by ferric salts. On the other hand, plant tests using sulfuric acid pickle liquors (an acidic solution of ferrous sulphate) gave just as good results in most cases as tests in which acidic ferric chloride solution was used.

In a study of the aqueous chemistry of slightly soluble iron compounds, Singer (1970) demonstrated some important facts about the behaviour of iron phosphates. Perhaps most significant is that the oxidation of ferrous to ferric ion is very slow in acid solution, but is very rapid in neutral or alkaline solution. The kinetic rate law followed at a pH above 5 is given by,

$$- \frac{d [\text{Fe}^{+2}]}{dt} = k [\text{Fe}^{+2}] [\text{OH}^-]^2 P_{\text{O}_2}$$

Values of the rate constant  $k''$  are shown in Figure 1, where

$$k'' = \frac{k}{2.3} [\text{OH}^-]^2 P_{\text{O}_2}$$

At pH values below 3.5, the reaction is reasonably independent of pH. The extreme dependence of the oxidation rate of pH in less acid solutions can be demonstrated by the fact that at 25°C and 0.20 atm of oxygen pressure, the half-life of the reaction (that is, the time to oxidize one-half the ferrous

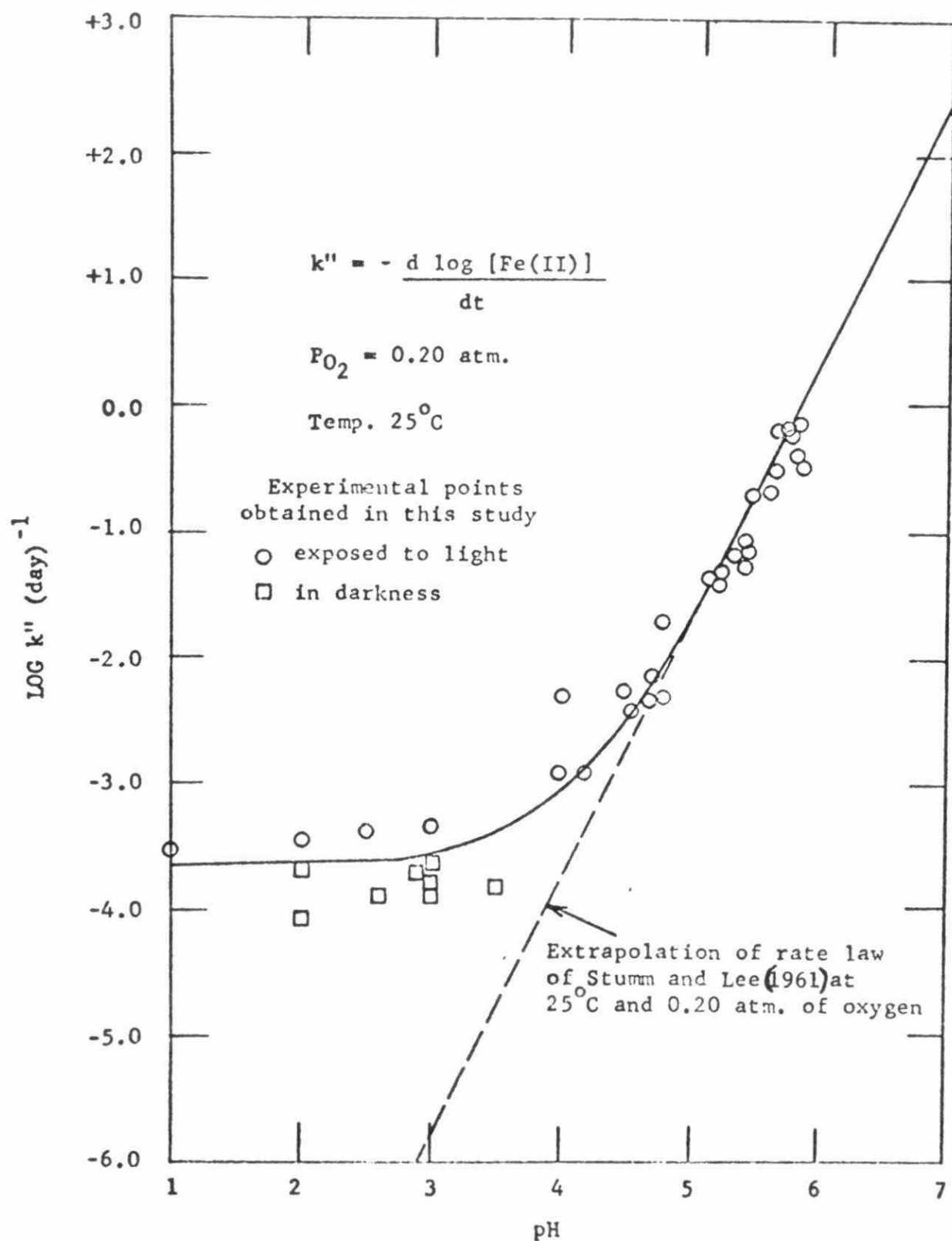
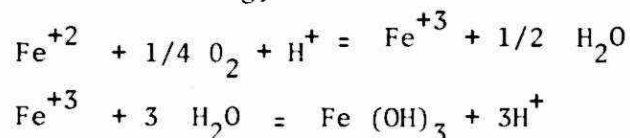


FIGURE 1 Oxygenation rate of ferrous iron as a function of pH.

ion to ferric) is about 2000 days at pH = 3.5, and about 4 minutes at pH = 7. In nearly neutral solutions, the iron is present largely as a hydroxide, the net oxidation reactions being,



Clearly, in any system having an adequate supply of oxygen (e.g. a ferrous iron addition of 25 mg/l to an aeration tank will probably cause less than a 5% increase in air requirements) and a pH of 6.5 or more, there will be a rapid conversion of iron from the ferrous state to the ferric. As a result conventional jar tests carried out using ferrous salt as a phosphorus removal chemical cannot be expected to be representative of plant performance, as the oxygen supply in a jar test is usually deficient, and the iron will tend to remain mainly in the ferrous state. In a treatment plant with adequate aeration, the iron quickly oxidizes to the ferric state. Therefore, results in which jar tests indicate that ferric salts are rather more effective than ferrous salts while pilot plant or field tests show little difference in effectiveness, are explainable on the basis of the rapid oxidation occurring.

It can be concluded, therefore, that in any treatment plant with adequate oxidation capacity and with pH around 7, iron salts may be added either in ferrous or ferric form with equal effectiveness.

This important point is further demonstrated by kinetic experiments carried out by Singer (1970). In these tests, a 15-minute reaction was allowed with an initial phosphorus concentration of  $10^{-4}$  moles/litre (3.1ppm as phosphorus). In Figure 2-A, iron was added directly as ferric ion together with sodium carbonate to maintain a constant pH, while in Figure 2-B, the iron was added as ferrous ion. In both tests, the solutions were aerated at a pH above 6, and ozonated at lower values of pH. The results show that a lower pH values (6.0 or less), ferrous ion oxidized in situ to ferric ion (what Singer calls homogeneous generation) was somewhat more effective for phosphorus removal than ferric ion added initially. However, at pH values of 6.5 or more, a considerable excess of iron over the stoichiometric is required for good phosphorus removal, and even this excess will not remove all the

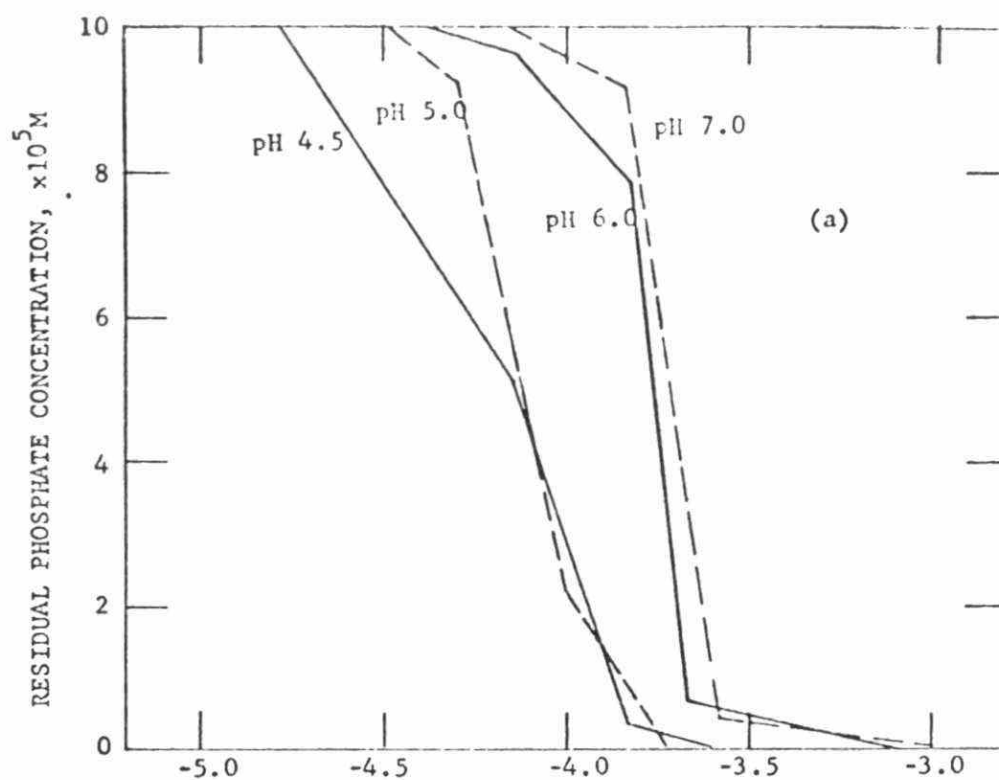


FIGURE 2A LOG [Fe(III)] APPLIED BY DIRECT ADDITION

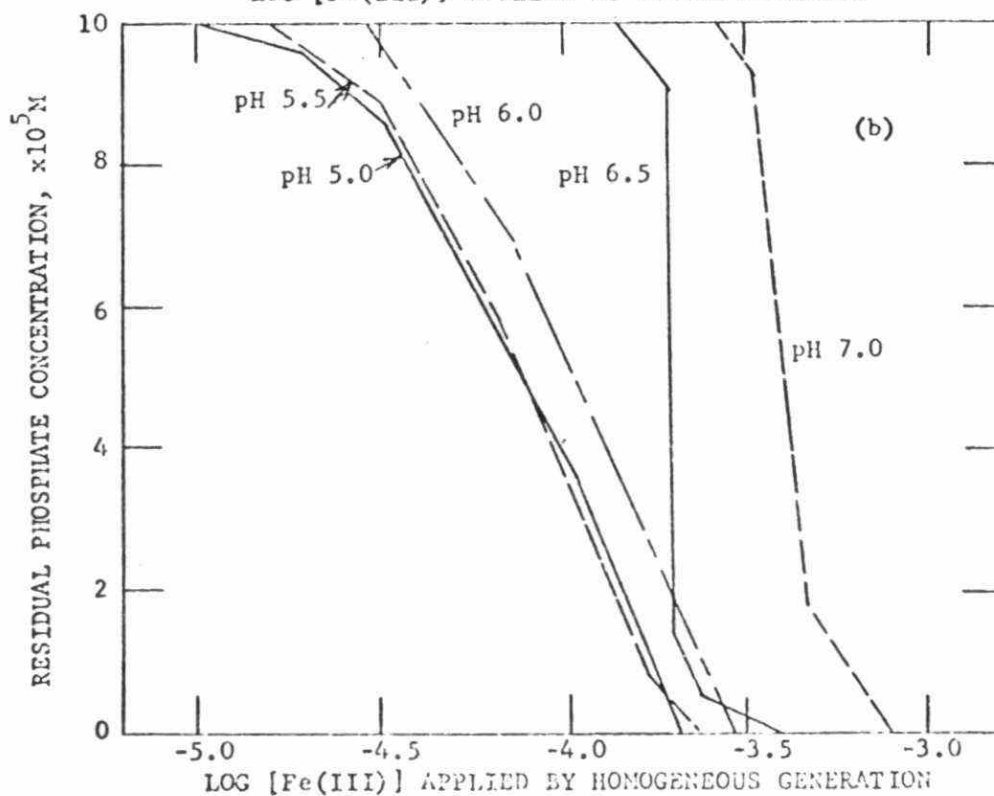


FIGURE 2B Precipitation of phosphate by (a) direct addition of Fe(III) and by (b) homogeneous generation of Fe(III).

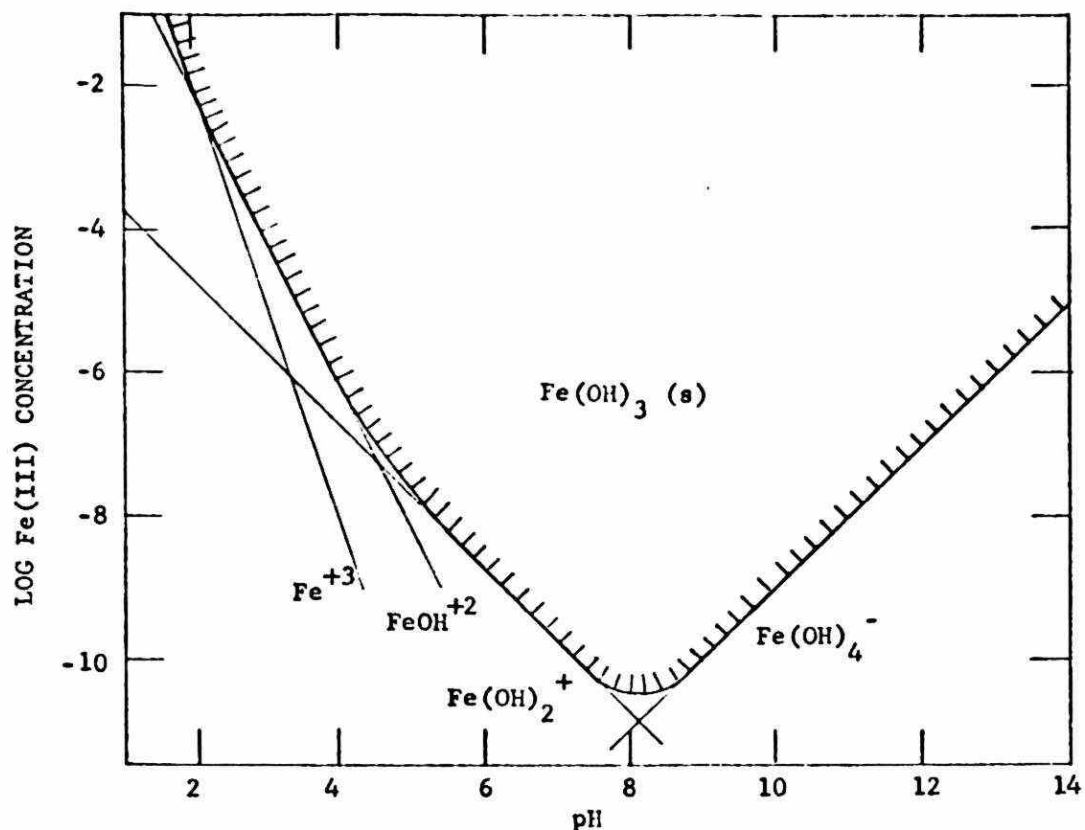


FIGURE 3 Solubility of ferric iron.

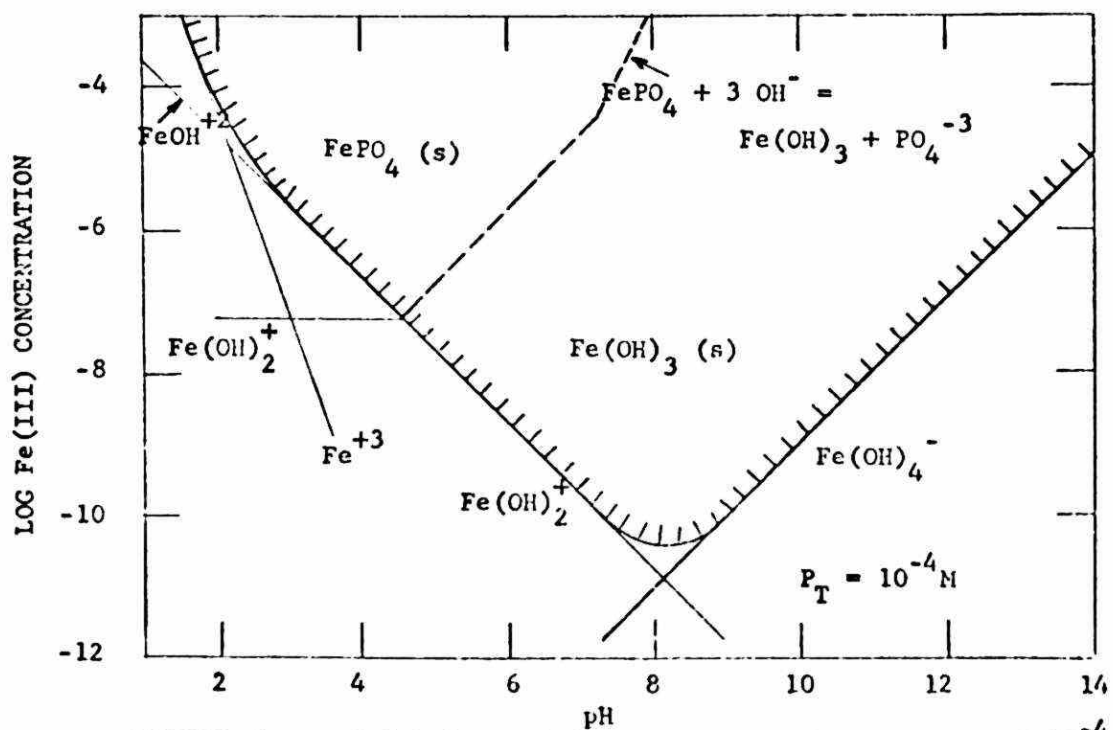


FIGURE 4 Solubility of ferric iron in the presence of  $10^{-4} \text{ M}$  of total phosphate species.



phosphorus in a reasonable time.

In Figure 3 is shown the solubility of ferric ion in an aqueous solution. The hatched line shows the regions of equilibrium between the ionic species indicated in solution and solid ferric hydroxide. Figure 4 shows the solubility of ferric ion in a solution originally containing  $10^{-4}$  moles/litre of total phosphorus. The upper part of the diagram shows the conditions of pH and soluble iron concentration under which the solid product formed will be ferric phosphate or ferric hydroxide. The lower parts of the diagram indicate the ionic form of the ferric ion existing in solution in equilibrium with the solid. At pH values above 4.5, the solubility of iron is controlled by the solubility product of ferric hydroxide rather than that of ferric phosphate. However, the solubility product of ferric phosphate is sufficiently low ( $\sim 10^{-24}$ ) that phosphorus is still reduced at equilibrium to the parts per billion level for most cases.

The above discussion applies to soluble phosphorus, presumably largely in orthophosphorus form, and therefore to only a part of the phosphorus removal which occurs on addition of iron salts to wastewater. In actual plant tests, the ferric hydroxide floc apparently settled reasonably well (although occasionally polymeric additives have been helpful), and yielded a relatively high density sludge.

## MARKET REQUIREMENTS FOR PHOSPHORUS REMOVAL CHEMICALS

The Government of Ontario through the Ministry of the Environment has established a program for the initiation of phosphorus removal processes in all Ontario treatment plants. This program calls for the installation of phosphorus removal facilities for all plants discharging into Lake Erie by December, 1973, and for most other treatment plants by December, 1975. The effluent quality requirement is generally set at 1 mg/l total phosphorus; however, in some areas 80% removal is required. A summary of the plant capacities, sizes and dates at which phosphorus removal treatment is scheduled to begin is shown in Table I. The total amounts of phosphorus removing chemicals required are shown in the Table also, assuming an average dosage and that the total requirement is met by iron salts, alum or lime, respectively, at this average dosage. The anticipated market requirements are shown graphically in Figure 5 in terms of exclusive use of iron salts for phosphate removal, and assuming a range of dosage from 10 ppm to 20 ppm of iron. In fact, operating practice suggests that some plants can treat successfully to meet the effluent quality requirement with as little as 8 ppm of iron and others require up to 25 ppm. The average large plant handling mainly domestic rather than industrial wastes would probably require dosages in the 10-15 ppm range. Therefore, a conservative approach would be to assume the market to be represented by a band between 10-15 ppm dosage, with an overall average of 12-13 ppm as probably reasonable in light of the reductions occurring in influent phosphorus concentrations at most treatment plants.

The foregoing data represents the total market for phosphorus removing chemicals. How the market will divide between lime, alum, and iron salts depends on the dosage of each required at a given plant, the cost of each, locally available supplies, and plant operator's preferences. A further analysis of the figures given in Table I shows that the Metropolitan Toronto treatment plants comprise just under 50 percent of the total capacity. Therefore, the distribution of the market depends strongly on the method to be used in these plants.

Table I

Probable Consumption of Phosphorus Removal Chemicals in Ontario Treatment Plants

Start-Up Date	Number of Plants	Total Capacity MGD	Owner			Type			Chemical Usage, Tons/year		
			O.M.E.	Munic.	P.P.U.D.	Prim.	Sec.	Lagoon	Lime at 250 ppm	Alum at 120 ppm	Iron at 15 ppm
December, 1973											
> 1.0 MGD	30	155.4	16	14	0	7	23	0	70900	34030	4250
< 1.0 MGD	72	20.5	23	13	36	3	28	40	9350	4490	560
December, 1975											
> 1.0 MGD	50	547.6*	18	31	1	15	34	1	249840	119920	14990
< 1.0 MGD	44	16.5	6	14	24	6	26	12	7530	3610	450
After 1975											
> 1.0 MGD	12	46.6	5	5	2	4	7	1	21260	10210	1280
< 1.0 MGD	145	41.1	39	42	64	15	53	77	18750	9000	1130

Plant data from private communications, and from Water and Pollution Control Directory, 1972-73, Southam Business Publications, Don Mills, Ontario

\*Metropolitan Toronto = 278 MGD

Lime as  $\text{Ca(OH)}_2$

O.M.E. - Ontario Ministry of the Environment

Alum as  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$

Munic. - Municipal

Iron as Fe

P.P.U.D.- Provincial Project under Development

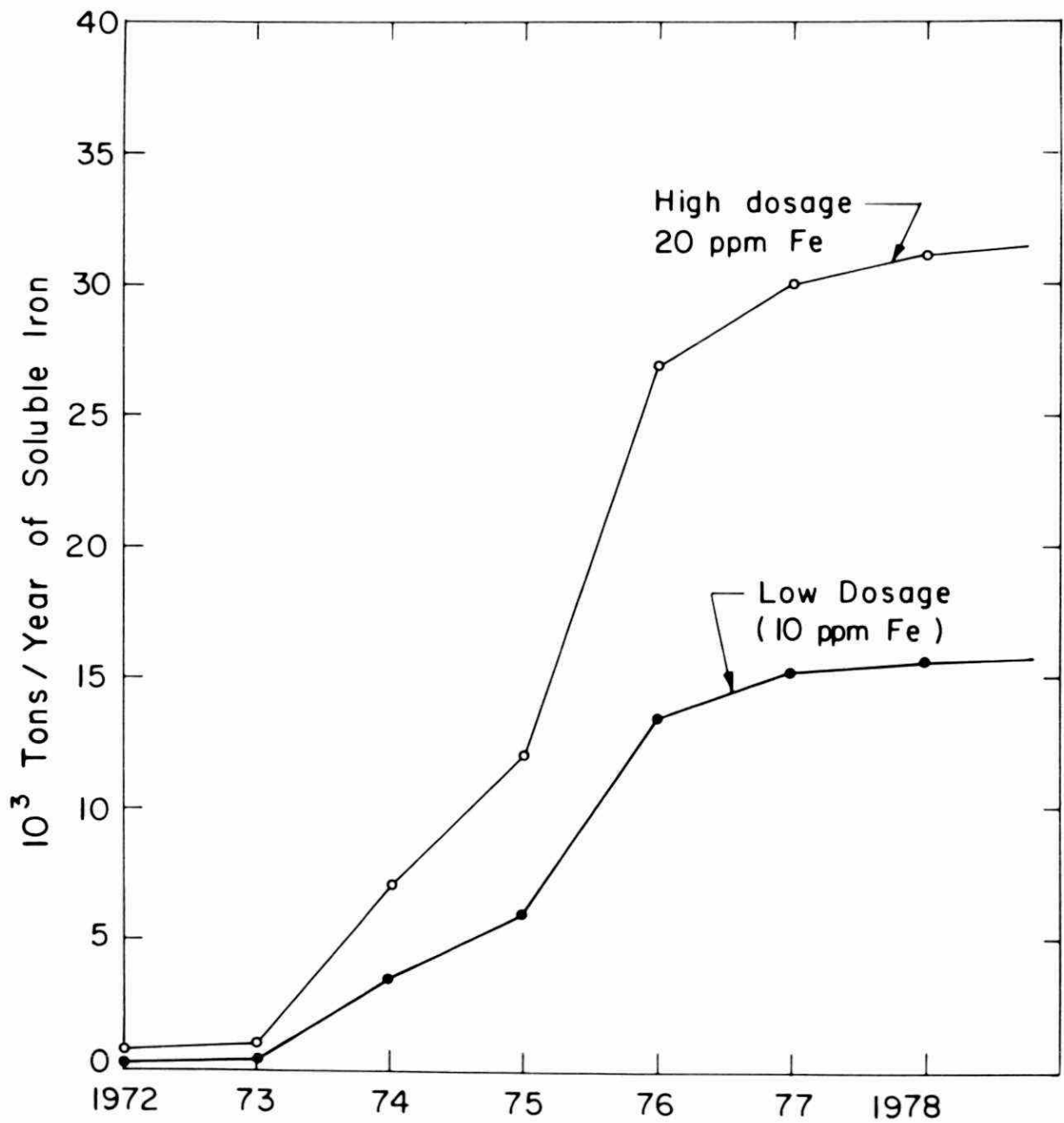


Figure 5 - Probable Total Consumption in Ontario of Chemicals for Phosphate Removal in Treatment Plants - Expressed in Terms of Soluble Iron

At the present time, most treatment plants prefer not to use a solid form of chemical because of the added inconvenience and cost of the storage, handling, and dissolving equipment. Since alum and iron salts are the chemicals most readily available as concentrated solutions, this factor rules out a widespread use of lime except in a few plants which have cheap local supplies, or special treatment problems. In addition, lime treatment leads to strongly alkaline sludges which are difficult to treat with conventional anaerobic digesters. The major choice is therefore between alum and iron salts, and the principal determining factor in this choice will be treatment cost per million gallons per day of capacity (\$/mgd). In process terms, alum or iron solutions are interchangeable, and a plant can be easily switched from one to another, which is not the case with lime.

One of the conclusions of this study is that the cost for phosphorus removal with iron salts can be significantly less than that using alum. On the basis of this conclusion, and on the basis of existing practice and avowed intentions of a number of plants, an estimate of the market for phosphorus treatment chemicals suggests that about 75 percent of the required chemicals will be iron salts; about 15 percent alum; and about 10 percent lime. The final estimate of the total Ontario market for iron salts for phosphorus removal is shown in Figure 6, as a single broken line. Within the limits of the previous conclusions, this prediction contains an uncertainty of 50 percent, due principally to the uncertainty in the overall average dosage level that will be used. There is a good probability that the line shown is no worse than 30 percent of the final market pattern. Also shown in Figure 6 is an estimate of the probable consumption of iron salts for phosphorus removal in the Toronto area, defined as a region within a 100-mile radius of Toronto.

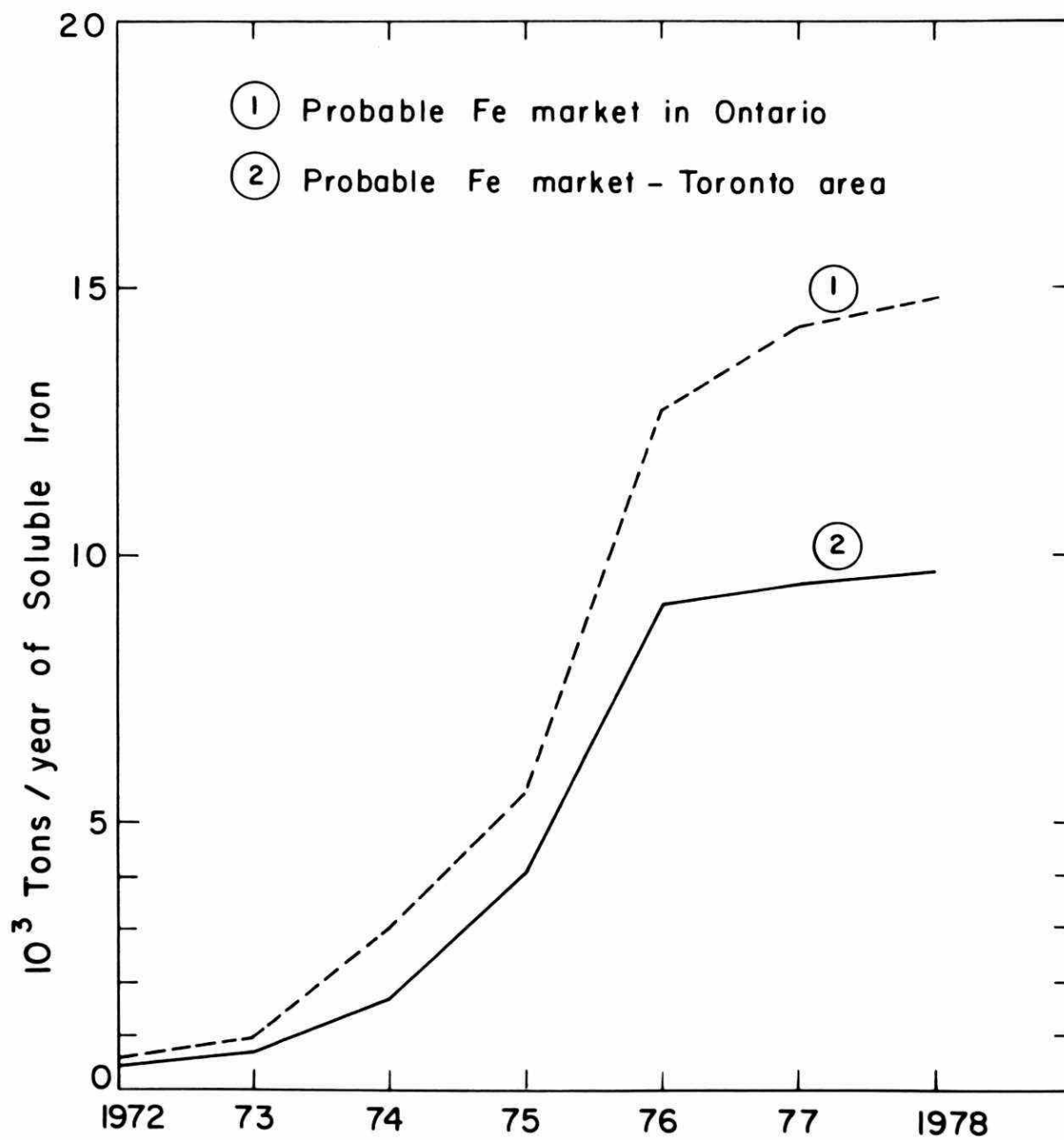


Figure 6 - Probable Consumption in Ontario of Iron Salts for Phosphate Removal. ("Toronto area" means within 100 miles)

## SOURCES OF IRON SALTS

### General

Because of cost considerations for the quantities needed for phosphorus removal, only four soluble iron salts need be seriously considered - ferrous chloride and ferrous sulfate, and ferric chloride and ferric sulfate. Ferrous chlorides or sulfates are often produced in Ontario as industrial waste by-products of various steel-finishing operations. It is also possible to manufacture either ferrous or ferrous salts from a variety of raw materials, many of which are also waste products. The iron-containing waste products may have iron in the ferric or ferrous form, and significant amounts of each are available. In general, when any of these iron-containing materials are treated with a strong acid, a salt of that acid will be formed. If there are not strong oxidizing conditions and the iron material is in elemental or ferrous form, then a ferrous salt will be obtained, but if the iron is in the ferric form, then a ferric salt will be obtained. It is, of course, also possible to purchase market grade raw materials such as acid and iron ore, or elemental iron, and manufacture a high-grade iron salt whose specifications can be closely controlled.

Ideally, if a source of iron salts of guaranteed quality is required, then the most desirable form of manufacture would be from specially purchased raw materials with the necessary quality specifications to insure an acceptable product. However, iron-containing waste materials are available in sufficient quantities to supply more than the requirements for iron salt manufacture. Further, many of these waste products involve present or future disposal problems for their producers. An obvious benefit to the provincial economy results, therefore, if these wastes can be consumed to produce a useful chemical for phosphorus removal. If this also involves the use of sulfuric acid, an additional small outlet is provided for the glut of sulfur produced in meeting pollution prevention requirements. It becomes necessary however, to assess the nature of these waste materials, and their major impurities to determine whether or not they can be tolerated in iron salts which may be used for phosphorus removal in sewage treatment plants.

### By-Product Iron Salts

The major by-product iron salts presently produced are either ferrous sulfate from sulfuric acid pickling of steel, and ferrous chloride from hydrochloric acid pickling of steel. The two largest producers of pickle liquor in Ontario are the Steel Company of Canada (Stelco), and Dominion Foundries and Steel Company (Dofasco) both of Hamilton. In recent years, these two companies have turned to hydrochloric acid pickling in order that the pickling process may be made into a closed loop with recovery and regeneration of the hydrochloric acid used. This process is now in successful operation at Stelco, and has recently been started up at Dofasco. The pickling operations of either of these two producers would yield enough soluble iron to satisfy most of the Ontario demand in the 1970's. However, with the successful implementation of acid recycling, these sources of soluble iron are no longer available.

A substantial number of smaller firms in the metal fabricating business produce quantities of pickle liquor, most of it ferrous sulfate in a solution of sulfuric acid. A typical pickle liquor might contain about 25-50 grammes per litre of iron and about 50 grammes per litre of sulfuric acid. Depending upon the nature of the manufacturing operation, this pickle liquor will be contaminated by varying amounts of zinc, manganese, copper, lead and nickel. The amounts of these minor metals in pickle liquor is so variable from plant to plant that if a knowledge of their content is needed, an analysis would be necessary for each source of liquor. As an economy move, and also to reduce environmental problems, many of the plants producing pickle liquor have installed equipment which crystallizes ferrous sulfate heptahydrate from spent pickle liquors and returns the unused acid to the process. The ferrous sulfate crystals produced are of quite a high purity, and the amounts of minor metal contaminants have been reduced.

Table II gives a list of some of the major sources in Ontario of ferrous sulfate heptahydrate crystalline material, as well as of sulfuric acid pickle liquor. In some locations, this material is given away to those who will remove it; other plants sell the crystalline product at a current price of about \$8 per ton of heptahydrate salt to pigment manufacturers who use it to produce ferric oxide pigments through a roasting process. Typical



Table II

Soluble Iron Production  
as Ferrous Sulphate

<u>Company</u>	<u>Location</u>	<u>Present Production+ (Tons/yr Fe)</u>	<u>Source</u>	<u>Product Form</u>	<u>Remarks</u>
Dominion Steel and Coal Co. (Dosco)	Toronto	590	Pickle Liquor	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Output goes to pig- ment manufacture
Sivaco Co. Ltd.	Ingersoll	360	Pickle Liquor	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	
Firestone Steel Co.	London	300	Pickle Liquor	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	
Motor Wheel Corp. of Canada Ltd.	Chatham	260	Pickle Liquor	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Output goes to pig- ment manufacture
91 P. L. Robertson Manufacturing Co.	Milton	40	Pickle Liquor	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Output bagged and sold
Wimco Steel Sales Co.	Rexdale	50	Pickle Liquor	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	
Atlas Steel Co.	Welland	14	Pickle Liquor	$\text{H}_2\text{SO}_4\text{-FeSO}_4$ soln + (50 gpl Fe)	
Steel Co. of Canada	Hamilton	200	Pickle Liquor	$\text{H}_2\text{SO}_4\text{-FeSO}_4$ soln + (36 gpl Fe)	
Algoma Steel Co.	Sault Ste. Marie	400	Pickle Liquor	$\text{H}_2\text{SO}_4\text{-FeSO}_4$ soln * (29 gpl Fe)	
North American Rockwell Co.	Chatham	55	Pickle Liquor	$\text{H}_2\text{SO}_4\text{-FeSO}_4$ soln * (30 gpl Fe)	
Lundy Steel	Dunnville )	18	Pickle Liquor	$\text{H}_2\text{SO}_4\text{-FeSO}_4$ soln	
General Steel Wares	London )				

Table II - Continued next  
page

Table II - Continued

<u>Company</u>	<u>Location</u>	<u>Present* Production+ (Tons/yr Fe)</u>	<u>Source</u>	<u>Product Form</u>	<u>Remarks</u>
General Wire and Cable Co.	Coburg	55	Pickle Liquor	H <sub>2</sub> SO <sub>4</sub> -FeSO <sub>4</sub> soln (47 gpl Fe) <sup>+</sup>	
East Side Plating Co. of Canada	Windsor	76	Pickle Liquor	H <sub>2</sub> SO <sub>4</sub> -FeSO <sub>4</sub> soln	
Canadian Titanium Pigments	Varennnes, Quebec	8300	Spent Acid	H <sub>2</sub> SO <sub>4</sub> -FeSO <sub>4</sub> soln (25 gpl Fe, 300 gpl H <sub>2</sub> SO <sub>4</sub> ) <sup>+</sup>	Waste Product

\*Single Sample Analysis

<sup>+</sup>Producer's Value

analyses of ferrous sulfate produced by crystallization from a sulfuric acid steel pickle liquor show purities of better than 99 percent, and usually the salt is about 99.5 percent  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Again, the quality of the heptahydrate will vary somewhat depending upon its source but it is unlikely that minor metallic elements would be present in amounts sufficient to cause concern. In Table III are given some pickle liquor analyses, which demonstrate the variable amounts of minor constituents occurring.

#### Imported Iron Salts

Just as ferrous sulphate and ferrous chloride are by-products of steel pickling operations in Ontario, they also represent waste products in the steel fabricating plants of the U.S. Great Lakes States. Ferrous sulphate, particularly, is available at the present time from these and other operations in crystal or solution form in very large quantities - much larger than the existing American market. Similarly, ferric chloride is available in large quantities from by-product acid, from leaching operations, etc. Of the four significant iron salts mentioned ferric sulphate is probably the only one not available in large tonnages from the United States as a waste product.

At the present time, ferrous sulphate is produced in Ontario, although not in the quantity required for phosphorus removal (see Table II), as well as a small amount of ferric sulphate (Electric Reduction Company, Port Maitland, Ontario). No ferrous or ferric chloride is manufactured in this province, although ferric chloride is readily available in quantity as an imported chemical from a number of distributors (e.g., Dow Chemicals, Pennsalt Chemicals).

With respect to importation of iron salts versus domestic production, the following facts cannot be too strongly emphasized:

1. An increasing glut of iron-containing waste products exists in Ontario of such a quality that the iron cannot easily be recovered as metal but from which soluble iron salts can be made.
2. A severe over-production of sulphur or sulphuric acid exists in Canada and will become worse, as additional sulphur removal is practised by a variety of industries.

Table III

Pickle Liquor Analyses

(Analyses by Wastewater Technology Centre, Canada Centre for Inland Waters,

Samples received July-August, 1972, Analysis dated September 14, 1972)

<u>Sample Source</u>		<u>Analysis</u>							
<u>Company</u>	<u>Location</u>	<u>Fe</u> <u>gms/litre</u>	<u>Al</u> <u>ppm</u>	<u>Cr</u> <u>ppm</u>	<u>Cu</u> <u>ppm</u>	<u>Mn</u> <u>ppm</u>	<u>Ni</u> <u>ppm</u>	<u>Pb</u> <u>ppm</u>	<u>Zn</u> <u>ppm</u>
Algoma Steel Company	Sault Ste. Marie	28.5	23.0	18.8	8.0	420	20.0	3.8	9.0
Atlas Steel Company (H <sub>2</sub> SO <sub>4</sub> liquor)	Welland	31.0	23.0	17100	2.6	200	1440	16.0	10.5
Interlake Steel	Thorold	0.7	6.0	9.5	2.0	9.0	7.2	3.0	57500
Lundy Steel	Dunnville	27.3	23.0	14.0	9.6	3500	24.8	4.0	13.0
N. American Rockwell	Chatham	29.8	40.2	9.0	3.5	116	18.6	9.2	8.6
Canadian Titanium Pigments (waste acid from TiO <sub>2</sub> plant)	Varenes, P. Q.	25.0	4250	280	4.0	210	8.4	5.3	10.0

3. Iron salts can be manufactured in Ontario in the quantities required at competitive prices to imported products, providing these imports are not dumped on the market, or subsidized in order to ease an American pollution problem.
4. There can be no economic benefit to the Canadian taxpayer in importing large quantities of iron and sulphuric acid or hydrochloric acid in the form of iron salts when Ontario is a major producer of these raw materials and many industries have pollution disposal problems involving waste iron and acid.

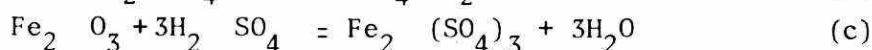
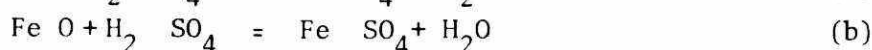
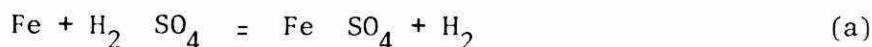
A real probability exists that Canadian chemical companies will be under pressure to import iron salts which are a waste product, or for which production capacity already exists in the United States. Even though such imports might be offered at marginally lower prices than domestically produced salts, any savings in sewage treatment costs would be lost many times over by the Canadian companies who lose these sales and who still must pay disposal costs for their own waste products.

In view of the low projected cost of manufacturing iron salts in Ontario, there can be no economic justification for the use of imported chemicals.

## MANUFACTURE OF IRON SALTS

In principle, the manufacture of iron salts is a simple operation. When a wide variety of iron-containing materials is treated with a strong acid, the iron dissolves to form a soluble salt. Since sulphuric acid is the cheapest strong acid, it will be assumed that a ferrous or ferric sulphate would be the likely product. Hydrochloric acid could be used equally well, given a competitive price, since it is not important whether a chloride or a sulphate salt is used for phosphorus removal.

The source of iron could be elemental iron from scrap, tin cans or sponge iron; iron in largely ferrous form such as mill scale, slags, etc., or; iron largely in ferric form such as iron ore, steel furnace fume, waste oxides, etc. Typical reactions which might occur would be:



If oxidizing conditions exist then another reaction also occurs in acid solution:



However, as pointed out previously, below a pH of 3.5 this reaction is kinetically so slow when air is used as an oxidant, that the amount of ferric ion formed from ferrous ion during the acid dissolution step would not be significant.

Reactions (a), (b), and (c) indicate that elemental or ferrous iron yields a ferrous salt solution and ferric iron will yield a ferric salt. From the viewpoint of phosphorus removal, either appears to be able to be used satisfactorily. From the viewpoint of manufacture, the principal differences would be in rate of solution of the iron, and in the solubility or freezing point of the salt solutions. In Figure 7, the freezing point curves of ferrous and ferric sulphates are shown, as is also the solubility curve for  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ . The solubility of ferric sulphate is uncertain in more concentrated solutions because of the existence of highly hydrated

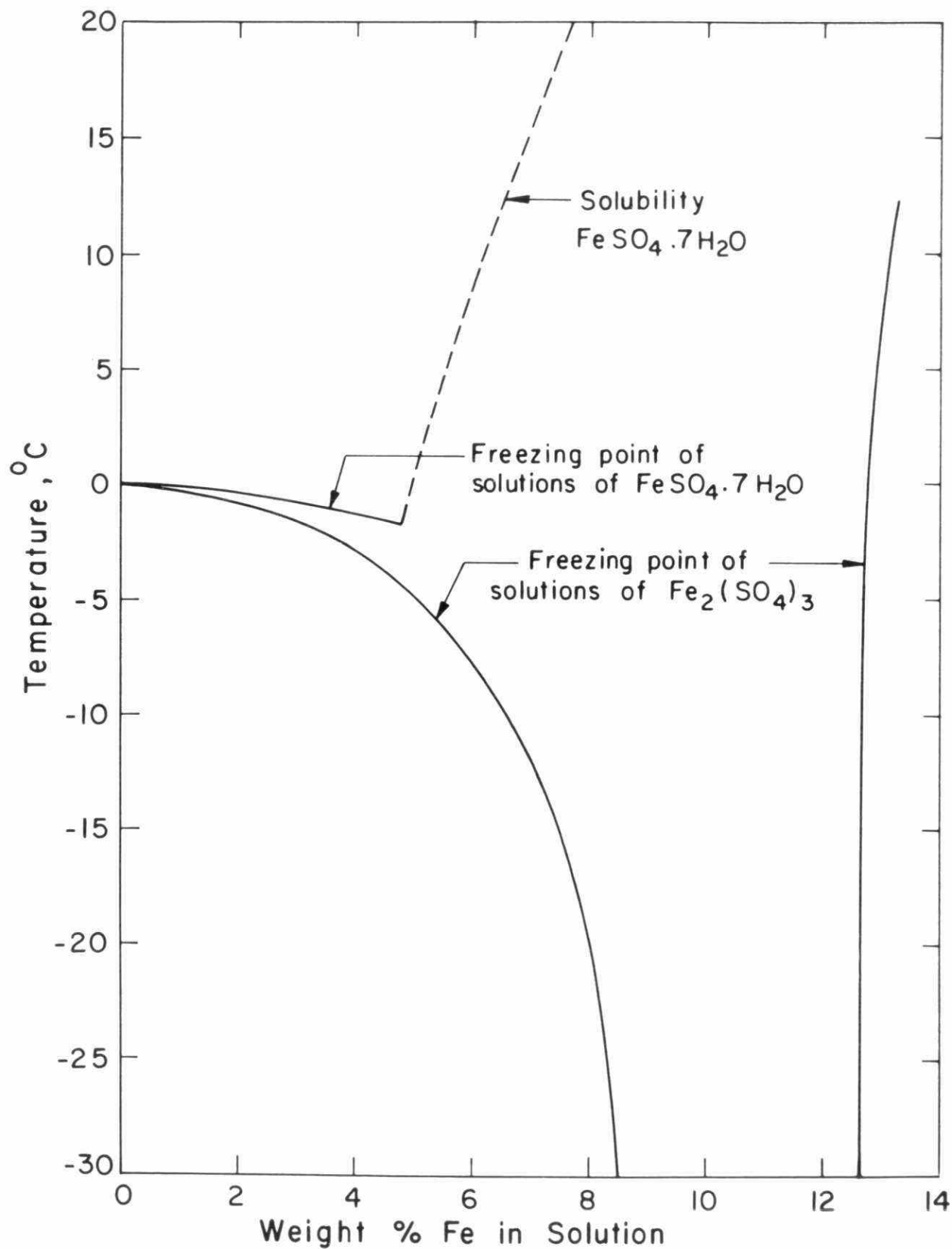


Figure 7 - Solubility and Freezing Points of Ferrous and Ferric Sulphates

( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  data from International Critical Tables;  $\text{Fe}_2(\text{SO}_4)_3$  data courtesy of Electric Reduction Co.)

forms, but for concentrations up to 12 percent by weight of iron, ferric sulphate may be considered to be completely soluble at all likely storage temperatures. (Ferrous and ferric chlorides are also very highly soluble, and solutions of about 8 - 10 percent by weight of iron can be stored at low temperatures.) However, the solubility of ferrous sulphate is much lower, and it decreases rapidly with temperature. Solutions stronger than about 5 percent iron cannot be stored at freezing temperature (less than 0°C). Operating difficulties have been reported when using ferrous sulphate pickle liquors in cold weather (Leary et al , 1972), because of the crystal formation in transfer lines, valves, etc., if these components are not heated. Many pickle liquors can contain from 5 - 8 percent by weight of ferrous iron in solution, and hence, crystallization may occur during storage or use in cold weather.

If an iron sulphate is to be stored and used in liquid form, then fewest problems would result if this product were a ferric sulphate. On the other hand, the acid consumption in manufacture would be less for a ferrous sulphate, and its potential purity might be higher, and these savings might offset the costs of storage in heated tanks.

In evaluating a process for iron sulphate manufacture, storage of raw materials and products will be a fairly costly item. Minimum storage needed depends on the proximity to raw materials and to markets. For a plant located in southern Ontario, iron and acid sources are nearby, as are the major markets (population centres). The Ontario Ministry of the Environment has adopted a general guideline of five days storage for treatment plant chemicals at a site, and since this represents a reasonable margin of safety, a minimum of five days supply of raw materials, and product storage equal to five days output will be used initially.

At least the following process units will be needed in a plant:

1. Acid storage - five days; probably 93 percent  $H_2SO_4$ .
2. Iron source storage - five days, probably open outdoor bulk storage.
3. Reaction Vessels - acid proof, design and type dependent on reaction.
4. Decantation or filtration.
5. Product storage - closed acid proof tanks.



Because of the corrosive nature of acidic ferrous or ferric salts, all equipment must be of acid-proof construction. If ferrous sulphate is the product, then product storage tanks must be insulated and heated.

The only process unit for which the design might not be entirely straightforward would be the reactor vessels. The rate of solution of iron by acid in these vessels will depend on the source of the iron, the acid concentration and temperature, and the solid surface area:mass ratio. The waste raw materials which might be useful vary widely in form, iron content, impurities, etc., but, in general, can be used interchangeably within certain limitations. One of the objectives of the present study was to evaluate the suitability of a number of these waste products as sources of iron for iron salt manufacture.

## IRON-CONTAINING WASTE PRODUCTS

Because of the variety of forms, sources and compositions of possible raw materials, a simple standardized rate-of-dissolution test was established to aid in preliminary evaluations. A quantity defined as "total recoverable iron" was determined by digesting a known amount of the solid in an excess of hot concentrated hydrochloric acid for two hours and then analyzing for iron. All total iron analyses were carried out using atomic absorption. Ferrous iron, when measured, was determined by dichromate oxidation in sulfuric acid solution using ferroin indicator. The "total recoverable iron" often represents essentially all the iron content of the solid, but in other cases, some iron is not readily acid soluble, and the "recoverable iron" result is significantly less than the total iron content (for example in Arvida red muds some iron is in the form of complex clays).

The standard leach test consisted of placing one litre of 1.4 N sulphuric acid in a round bottom two-litre flask equipped with an efficient stirrer and air agitation. The flask was then heated in a water bath to  $76^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , and a weighed solid sample was added. The solid was previously analyzed for "total recoverable iron", and the sample weight was calculated so that the acid was in at least 100 percent excess of the stoichiometric requirement. Samples were withdrawn periodically and analyzed for total iron, and sometimes for ferrous iron also, and the results expressed as the fraction of total recoverable iron dissolved (that is, as a conversion).

This standardized leaching test, using hot dilute acid, very clearly showed up differences in dissolution rates. Although the initial iron:acid ratio was reasonably constant, sample size varied widely because iron contents of various materials varied from 4 percent to 90 percent. Similarly, surface area:mass ratios varied widely, for the materials were used in the form in which they were produced and available, except in a few cases where this clearly would not have been a feasible plant practice, e.g., with pelletized material.

The materials tested and some details concerning the source and nature of each of the samples are given in the next chapter. The results of the standard leaching tests are shown in Figures 8 to 12, with materials identified by the same sample number as in the listing. Because one of the most important characteristics of the source of iron is whether on dissolu-

tion in sulphuric acid it will yield mainly a ferrous or mainly a ferric sulphate, the materials have been divided into these two primary classifications in the list. However, leaching tests shown in graphs are not necessarily grouped in this way, but often grouped according to source. The varying time scales in the plots should be noted also. The significance of the leaching tests and any special aspects of these tests are discussed as part of the description of each sample.

Differences in composition values given arise from three sources. Analyses for similar samples or from plant production data were supplied for many of the materials by the producers. These values are reported as "producer's analysis". A second value is also given for all materials on which dissolution tests were done as "total recoverable iron", and it is this value on which experimental conversions were based. Finally, differences in iron-content analyses also arise because producers' values are frequently long-term averages, whereas our values of "total recoverable iron" are based on samples from a particular day of operation. All compositions are reported on a dry solids basis as weight percent.

Commercial values given for these materials are usually producers' estimates, but in all cases are given only as a guideline. Actual value depends on negotiation.

## POTENTIAL SOURCES OF IRON

### Materials Yielding Primarily Ferrous Salts

(Excluding pickle liquors and crystalline  $\text{Fe SO}_4 \cdot 7 \text{H}_2\text{O}$ )

#### 1. Mill Scale - Burlington Steel Company, Hamilton.

Produced from hot-rolling operations. Large chunks to fine particles.

Mixture of  $\text{Fe O}$  and  $\text{Fe}_2\text{O}_3$  (approximately).

- Producer's Average Analysis: 72 percent Fe
- Our Sample: 77 percent recoverable Fe
- Production Rate: 3000 tons/year
- Probable Value: \$4 - \$10/ton F.O.B. plant

Standard leaching of material screened to -20 mesh gave only 15 percent conversion in three hours (Figure 10, line 1). The same material was also leached in  $5.9 \text{ N H}_2\text{SO}_4$  at same temperature (Figure 10, line 1A), and in three hours gave 63 percent conversion, suggesting that rate of dissolution is approximately directly proportional to acid strength. In hot concentrated  $\text{HCl}$ , the material dissolves rapidly and completely. The product is about  $2/3$  ferrous and  $1/3$  ferric sulphate.

#### 2. Slag - Electric Furnace - Burlington Steel Company, Hamilton.

After separating out metallic iron, slag is crushed and sized, and sold as special fill (-3/8 inch, or 3/8 inch to 6 inch size range).

- Producer's Analysis: 9.7 percent Fe, 6.0 percent Mn
- Production Rate: 22500 tons/year
- Probable Value: \$2/ton, F.O.B. Hamilton.

No leaching tests done.

#### 3. Mill Scale - Steel Company of Canada, Hamilton.

Produced in various plants from fabricating operations, in various degrees of fineness.

- Producer's Analysis : 72 percent - 80 percent Fe
- Production Rate: Very large
- Probable Value: Mill scale is returned direct to furnaces or sent

to sinter plant where furnace feed is prepared. Could be made available at a price competitive with clean scrap or other high iron, low impurity source. (Clean scrap is currently about \$45/ton in Hamilton.) The above analysis and comments also apply fairly well to the bulk of mill scale produced at Dominion Foundries and Steel Company (Dofasco) in Hamilton.

No leaching tests done.

4. Fine Mill Scale - Dofasco Limited, Hamilton.

A small fraction of total mill scale production. Produced in final hot rolling operations. Heavily contaminated with oil. Not recycled to furnaces but presently stock-piled.

- Producer's Analysis: 74 percent total Fe
- Our Sample : 71.4 percent total Fe recoverable, (50.3%,  $\text{Fe}^{2+}$ , 21.1%  $\text{Fe}^{3+}$ )
- Production Rate: 7200 tons/year
- Probable Value: about \$8/ton, F.O.B. plant

Standard leaching tests carried out using 20 gramme sample previously washed with detergent and rinsed to remove oil. Results are shown in Figure 8, line 4. In three hours, about 52 percent conversion occurred, of which about two-thirds was ferrous iron and one-third ferric iron. Higher rates of dissolution are due to fine particle size.

5. Foundry Waste - Ford Motor Company of Canada, Windsor.

Sludge resulting from wet scrubbing of stack gases. Available as sludge from settling basin.

- Producer's Analysis: Total iron - 12.3 percent  
(Mixture of Fe, FeO,  $\text{Fe}_2\text{O}_3$  = 29.2 percent)  
Balance mainly Si  $\text{O}_2$  = 49 percent  
 $\text{Al}_2\text{O}_3$  = 8 percent; CaO = 11 percent
- Our Sample: Total iron - 10.0 percent
- Production Rate: 4100 tons/year
- Probable Value: No commercial value

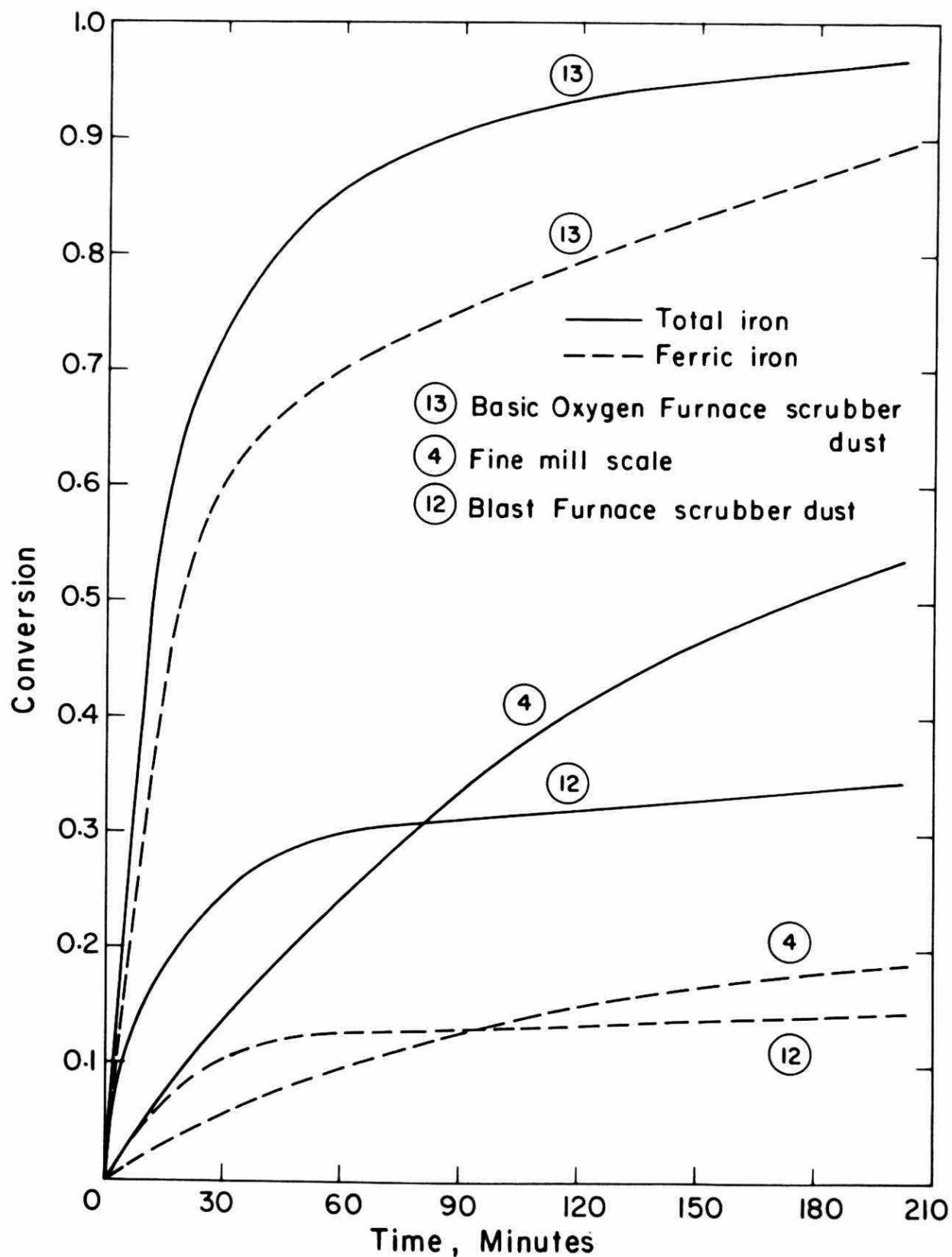


Figure 8 - Dissolution Tests, Standard Conditions, Samples from Dominion Foundries and Steel Co. (Dofasco), Hamilton

Standard leaching tests were carried out using sludge screened to -20 mesh. results are shown in Figure 10, line 5. Dissolution rates even in this dilute acid solution were rapid, and nearly 90 percent conversion was obtained in one hour, and 95 percent in three hours. Majority of product was in ferrous form.

6. Slag from Non-Ferrous Metal Reverbatory Furnace - (Company name withheld by request), Toronto.

Product normally produced in large chunks.

- Producer's Analysis: 31.1 percent total Fe,  
Si O<sub>2</sub> 25 percent; Ca O 15 percent
- Our Sample: 25.4 percent Fe recoverable
- Production Rate: 810 tons/year
- Probable Value: No commercial value

Standard leaching tests were carried out on crushed material with a sample of 20 grammes of -60 + 200 mesh. Results are shown in Figure 9, line 6. About one-half of the recoverable iron dissolved very quickly in a few minutes, and over 80 percent was dissolved in one hour. However, only about 84 percent conversion could be attained in dilute acid even at a long dissolution time. The product was nearly entirely in the ferrous form.

7. Matte from Non-Ferrous Metal Reverbatory Furnace - (Company name withheld by request), Toronto.

Product normally produced in large chunks; is mainly a ferrous sulphide.

- Producer's Analysis: Total Fe 46.6 percent;  
Sulphides and Sulphates 25 percent; Pb 5 percent
- Our Sample: Total Recoverable Fe 40.5 percent
- Production Rate: 1000 tons/year
- Probable Value: No commercial value

Standard leaching tests were carried out on crushed material using 20 grammes of -60 + 200 mesh. Results are shown in Figure 9, line 7. In three hours, about 41 percent conversion was obtained. At the start of the reaction, a considerable amount of H<sub>2</sub>S gas is given off. The product was nearly entirely in ferrous state.

8. Waste Tin Cans - Metro Toronto Solid Waste Disposal.

A planned operation magnetically separates out tin cans from solid wastes, and cans are then shredded (if necessary). No cleaning, burning, etc. is done.

- Producer's Analysis: None - not yet in production but assumed 95 percent + metallic iron
- Production Rate (estimated): 25000 tons/year

No leaching tests done. Cans must de-tinned before recycling to steel plant is feasible. De-tinning probably is not necessary for iron salt production. Product would be in ferrous form.

9. and 10. Sponge Iron from Iron Ore, produced from iron ore pellets by reduction in laboratory of pellets from Iron Ore Company of Canada (9), or from iron ore pellets reduced in pilot plant rotating kiln by Steel Co. of Canada (10).

- Producer's Analysis: 80 - 90 percent Total Iron content
- Our Sample (I.O.C.C.): 82 percent recoverable iron
- Production Rate: No sponge iron is currently produced in Canada on a continuous plant scale. However, Sidbec-Dosco will shortly start up first Canadian production at its plant at Contrecoeur, Quebec, and Stelco is planning future production in Ontario.
- Probable Value: Commercial value would be equivalent to scrap

Leaching tests were done on both kinds of reduced pellets. Pellets were crushed and samples of -18 +20 mesh used for dissolution test. Results are shown in Figure 12, line 9-10. Essentially, complete solution in the dilute acid occurred in about fifteen minutes.

The product was largely in ferrous form. The initial reaction was rather violent. These sponge irons, together with commercial iron powder, were the most reactive materials tested.

Materials Yielding Primarily Ferric Salts

11. Fume from Electric Furnaces - Burlington Steel Company, Hamilton.

Fumes from electric furnaces, which operate with a high percentage of scrap



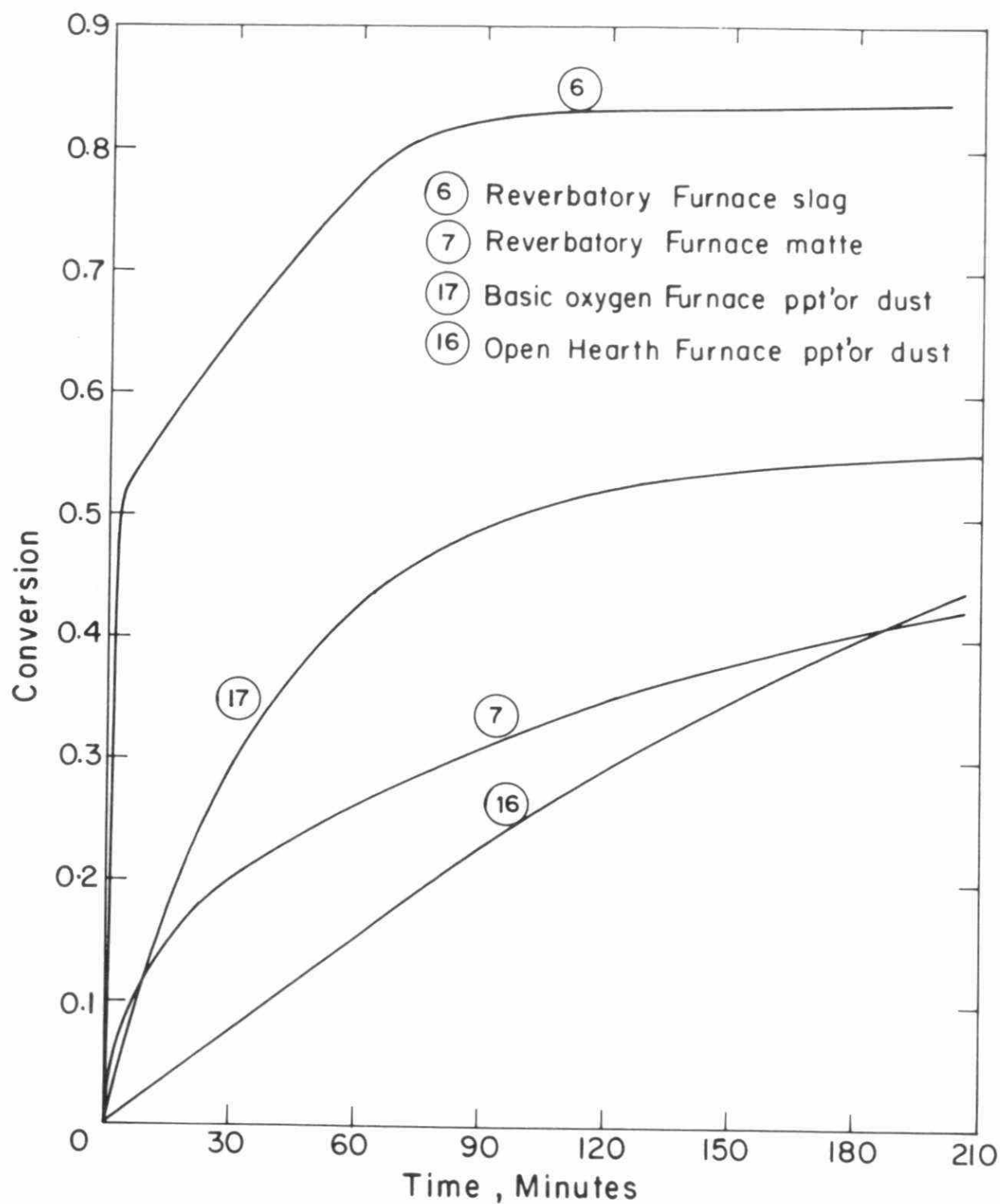


Figure 9 - Dissolution Tests, Standard Conditions, Samples from Steel Co. of Canada, and from a non-ferrous metal reverbatory furnace

in the charge, contain a wide mixture of metallic and non-metallic substances. Dust is recovered from bag houses and is very fine (e.g., -200 mesh). Similar dusts are produced from all electric furnace steel-making operations.

- Producer's Analysis: Total Iron 24.8 percent,  
Zn 9.4 percent, Al 4.4 percent
  - Production Rate: 800 tons/year
  - Probable Value: No commercial value at present
- No leaching tests carried out.

12. Blast Furnace Dust - Dofasco Ltd., Hamilton.

Dust from blast furnace is collected in dry separators (coarse dust) and wet scrubbers (wet dust). Dry coarse dust is lower in iron content and higher in carbon. Dust is a mixture of ore, partially reduced ore, coke and flux. Fine wet dust is mainly -325 mesh. Only the wet fine dust is considered further.

- Producer's Analysis: Total Iron 44.7 percent,  
C 14.8 percent,  
Zn 0.15 percent,  
Mn 0.35 percent,
- Our Sample: Recoverable Iron 39.4 percent
- Production Rate: 43800 tons/year
- Probable Value: At present, about \$8/ton. However around 1975, Dofasco will build a sinter plant, and this material can become part of sinter plant feed.

Leaching tests are shown in Figure 8, line 12. The material is not very reactive (e.g. iron ore, sample 20) and in three hours only 34 percent conversion occurred. The ferric content is also shown and after an initial period it parallels the total iron dissolution curve. From these results it would appear that about 15 - 20 percent of a final product would be in ferrous form and the balance in ferric form.

13. Fume from Basic Oxygen Furnace - Dofasco, Hamilton.

Basic oxygen furnace produces a fume (mainly  $\text{Fe}_2\text{O}_3$ ) which is removed in a two stage scrubber, one of which removes coarse grit (about 10

percent of total) and a second which removes fine particles (-200 mesh). The grit is a little higher in iron and lower in zinc than the fine material. Only the fine material is reported on below. It is available as a partially dried product from rotary driers, and may in future be available as filter cake.

- Producer's Analysis:                      Total Fe 55.2 percent,  
   Zn 3.92 percent,  
   CaO 5.9 percent,  
   Mn 0.31 percent,  
   C 0.62 percent
- Our Sample:                                Total Recoverable Fe 38.8 percent, Zn  
   3.52 percent, (Total Fe after 3 hours  
   in HCl - 49.4%, about 5/6 in ferric  
   form)
- Production Rate (Dry Basis):        43800 tons/year
- Probable Value:                        At present, valued at about \$6/ton.  
   This material is not as desirable a  
   feed for recycling because of its  
   higher impurity content, particularly  
   zinc.

Standard leaching test results are shown in Figure 8, line 13. Dissolution rates were high, with about 88 percent conversion in one hour and 96 percent conversion in 3 hours. Most of the product is in ferric form, with only 10 - 15 percent of the soluble iron as ferrous iron.

14. Regenerator Oxide - Dofasco Ltd., Hamilton.

( see also Sample 15).

The closed loop HCl pickling process employed by both Dofasco and Stelco has as its final step the regeneration of HCl from  $\text{FeCl}_2$  liquor in a fluidized bed roaster. A high purity ferric oxide is produced from the roaster, which will be  $\text{Fe}_2\text{O}_3$  plus all the metallic impurities in the pickle liquor (mainly manganese). Material is in form of small pellets (1 - 5 mm.).

- Producer's Analysis:                      Total Fe 69.0 percent
- Production Rate:                        7300 tons/year

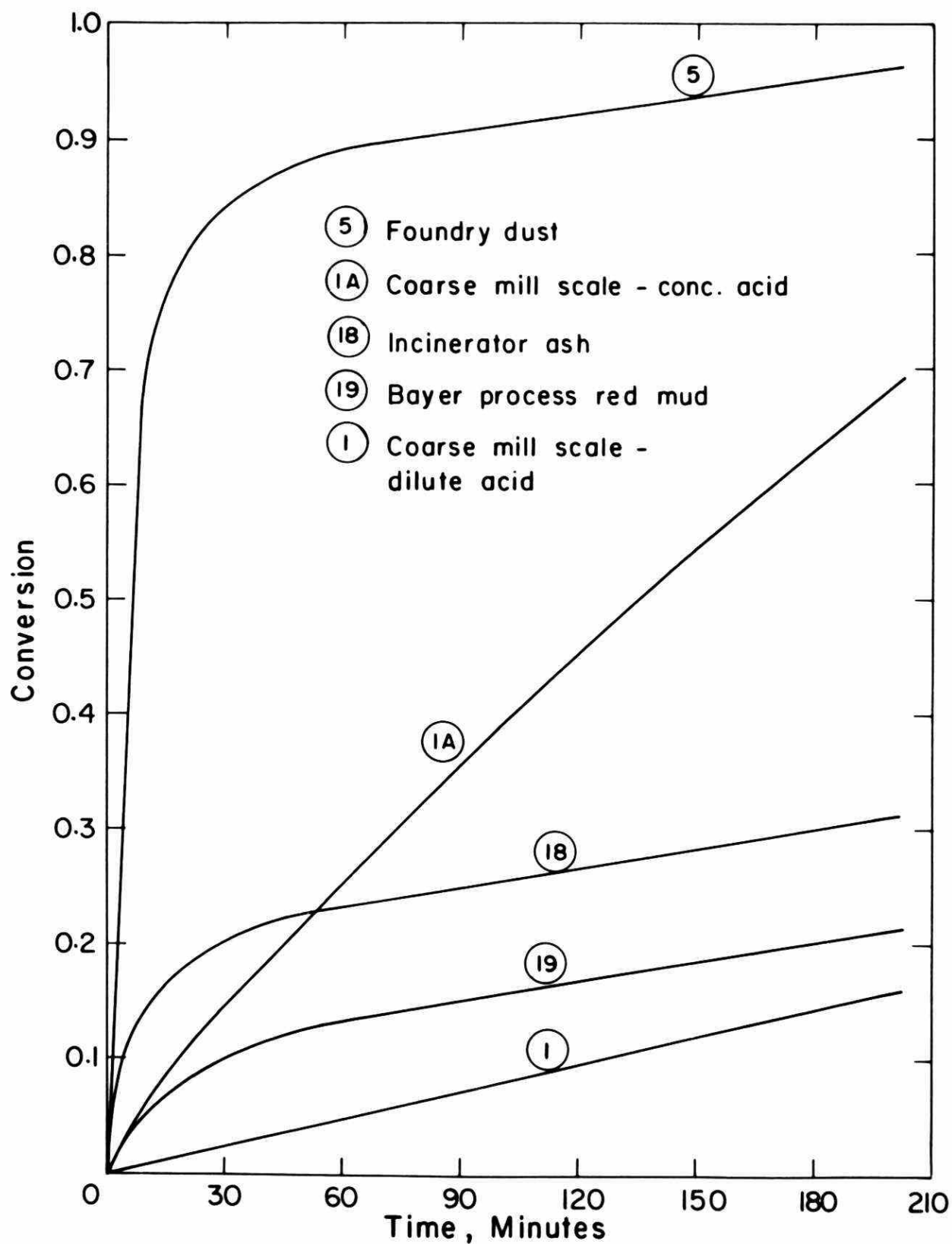


Figure 10 - Dissolution Tests, Various Samples,

Dilute acid - 1.4 N  $\text{H}_2\text{SO}_4$

Concentrated acid - 5.9 N  $\text{H}_2\text{SO}_4$

- Probable Value:                      Some limited market exists in pigment industry and ferrite industry. Value depends on negotiation, but presumably at least equal to high grade iron ore.

Standard leaching test showed behaviour very similar to iron ore (hematite - see Figure 11).

15. Regenerator Oxide - Steel Co. of Canada, Hamilton

Essentially same material as sample 14, although Stelco and Dofasco processes are not identical.

- Producer's Analysis:                      69 percent total Fe
- Production Rate:                          11000 tons/year
- Probable Value:                            As for Sample 14

Leaching behaviour as for sample 14.

16. Open Hearth Furnace Dust - Steel Co. of Canada, Hamilton

Fume (mainly  $\text{Fe}_2\text{O}_3$ ) collected in electrostatic precipitators from open hearth steel furnaces. Very fine dust (-325 mesh) readily goes to aerated flowable state, can also compact to 30 percent of aerated volume and become set. Abrasive, difficult to handle when dry. Can be slurried if over 30 percent water added.

- Producer's Analysis (average): 63.9 percent total Fe
  - CaO 0.7 percent
  - Zn 2.35 percent
  - Pb 0.46 percent
- Our Sample:                                69.5 percent recoverable iron
- Production Rate:                          75000 tons/year
- Probable Value:                            Mostly committed to land fill. Some sold to various buyers, probable price \$5 - \$10/ton FOB Hamilton. Stelco has severe logistics problem in trucking wastes from plant site, which may lead to extra expense. Material is not recycled to sinter plant.

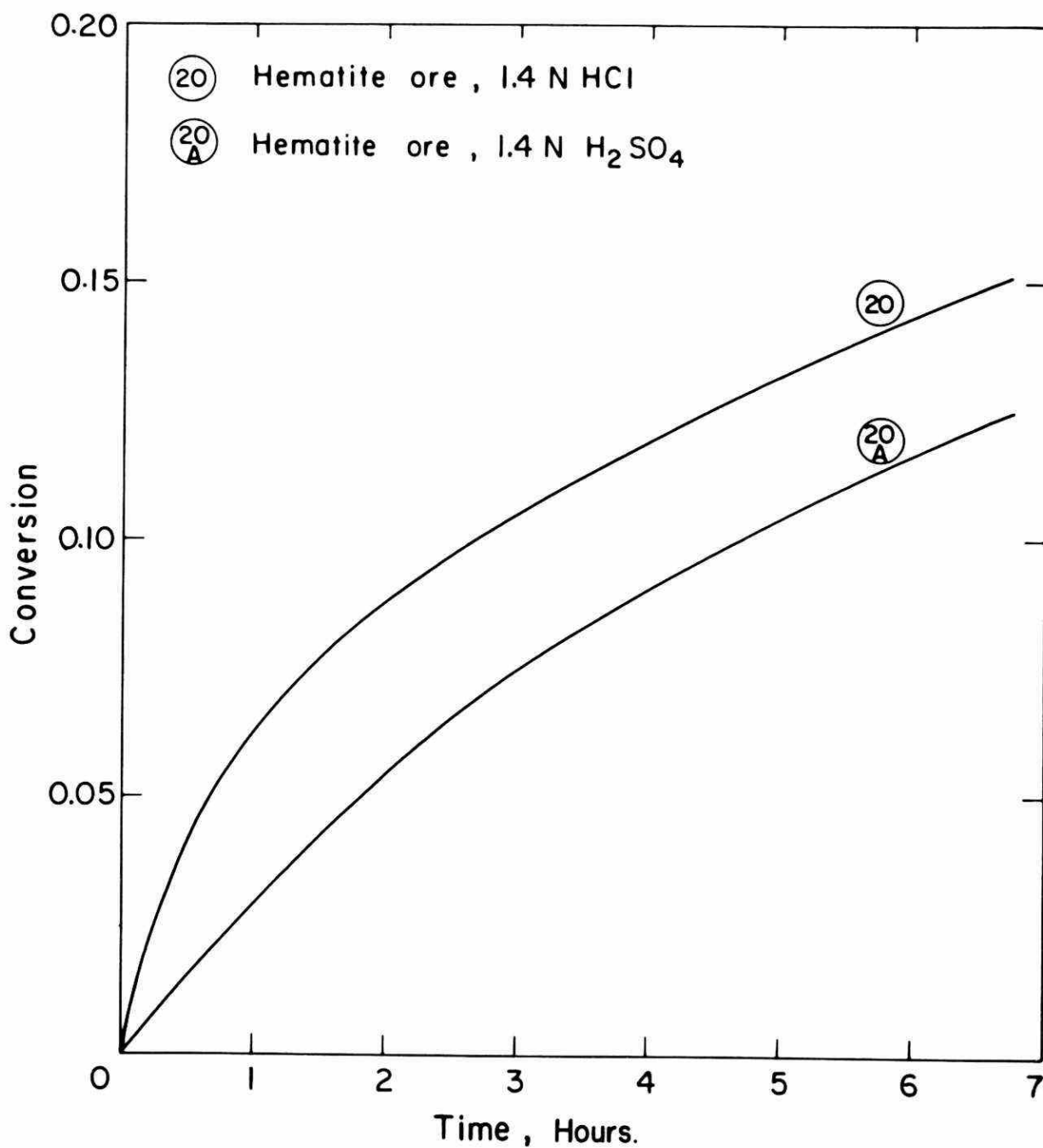


Figure 11 - Dissolution Tests, Hematite Ore, Standard Conditions,  
Samples from Iron Ore Co. of Canada

Standard leaching tests were carried out on 20 gram samples "as received", and results are shown in Figure 9, line 16. About 40 percent dissolution occurred in 3 hours in the dilute acid. In concentrated acid the dust dissolved rapidly and completely. Product was nearly entirely in the ferric form.

17. Fume from Basic Oxygen Furnace - Steel Co. of Canada, Hamilton .

Dry dust (mainly  $\text{Fe}_2\text{O}_3$ ) recovered from electrostatic precipitators. very fine, hard to handle, behaviour generally like sample 16.

Material not recycled to sinter plant.

- Producer's Analysis (average): 52.4 percent total Fe
  - CaO 6.9 percent
  - Zn 3.35 percent
  - Pb 1.33 percent
- Our Sample: Total recoverable Fe 55.4 percent
- Production Rate: 75000 tons/year
- Probable Value: As for sample 16

Standard leaching tests were carried out using 20 grams of the sample "as received". Results are shown in Figure 9, line 17. The initial rate of dissolution was high but it then slowed down with about 55 percent conversion in three hours. These results may be compared to line 13, Figure 8. The slower rate observed for sample 17 may be due mainly to a coarser size fraction in this material which has been removed from sample 13. On cooling the solution from the leaching of sample 17, a white crystalline precipitate, identified as  $\text{PbSO}_4$ , was formed. The soluble iron was nearly entirely in the ferric state.

18. Incinerator Ash - Ashbridges Bay Incinerator, Metro Toronto .

Ash resulting from combustion of sludge from main treatment plant of Metro Toronto (180 million gals/day).

- Producer's Analysis (average) : Total Fe 3 - 5 percent
  - $\text{Al}_2\text{O}_3$  20 percent
  - Zn 2 - 3 percent
  - Pb 0.5 percent
- Our Sample: Total recoverable Fe 4.8 percent

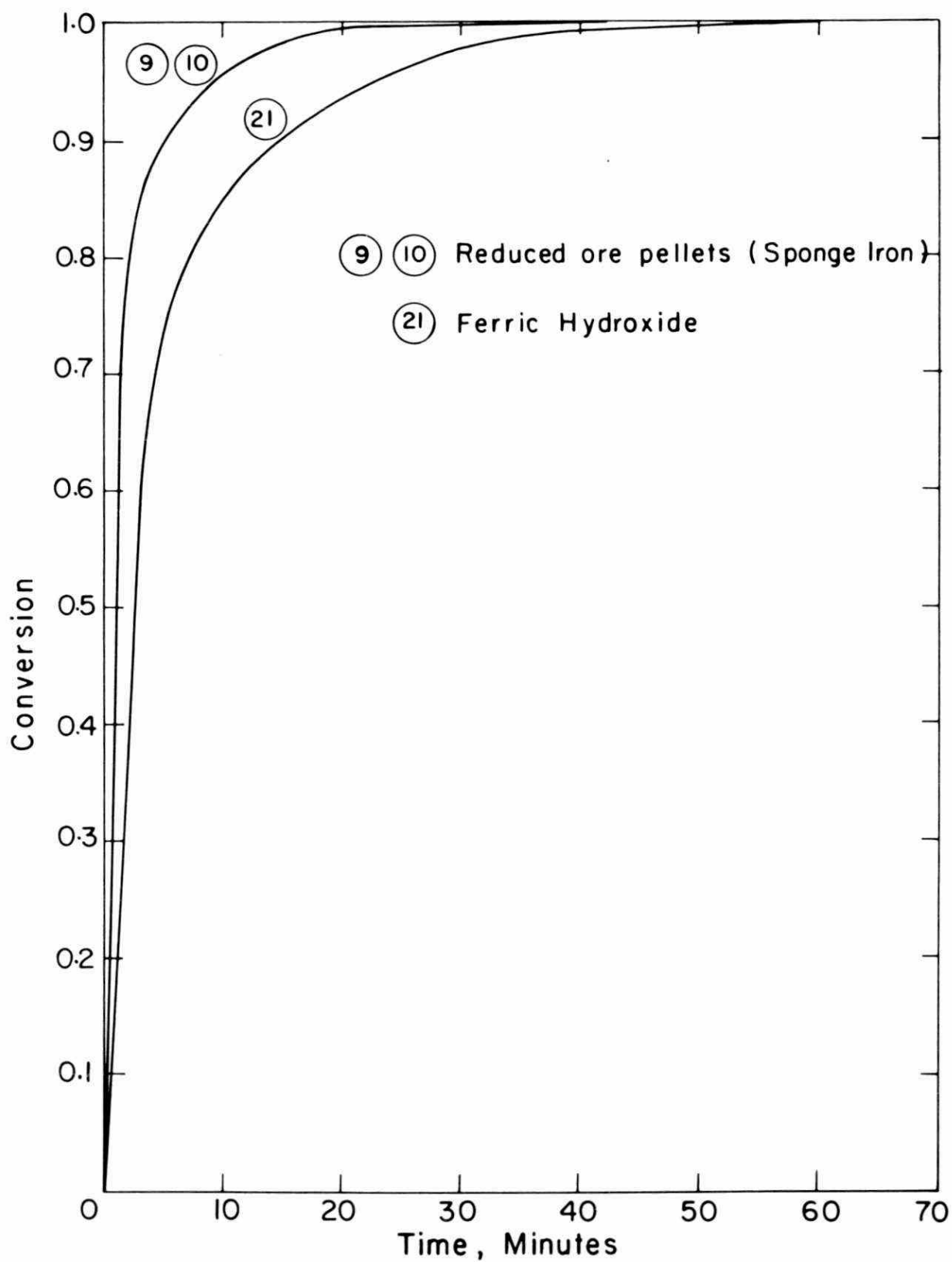


Figure 12 - Dissolution Tests, Special Materials, Standard Conditions,  
Sponge iron pellets from Iron Ore Co. of Canada pellets, and  
from Stelco pellets.  
Ferric Hydroxide - laboratory grade



- Production Rate (estimated): 21900 tons/year
- Probable Value: No commercial value

Standard leaching tests were carried out on 25 gram samples of solid screened to -20 mesh. Results are shown in Figure 10, line 18.

About 25 percent of the iron dissolves very rapidly, but the balance is less reactive and a total of about 30 percent dissolved in 3 hours. Product was largely in the ferric form.

19. Bayer Process Red Mud - Aluminum Co. of Canada, Arvida, Quebec

This material is the waste from the process for preparing pure alumina from bauxite ores. It is of interest primarily because of the immense quantities available. The "red mud" is an alkaline material containing complex sodium alumina silicates and complex iron compounds.

- Producer's Analysis (average): 10.0 - 12.5 percent total Fe  
Approximately 16 percent  $\text{Al}_2\text{O}_3$   
 $\text{SiO}_2$  19.4 percent  
 $\text{TiO}_2$  10 percent
- Our Sample: Total recoverable Fe 4.0 percent
- Production Rate: About  $10^6$  tons/year
- Probable value: No commercial value FOB Arvida.  
Shipment cost approximately \$22/ton to  
Toronto

Standard leaching test results are shown in Figure 10, line 19. Even though only a minority of the total iron appears to be in acid-soluble form, even this fraction of the iron does not dissolve readily. After 3 hours only 20 percent conversion had been obtained in dilute acid.

20. Hematite Ore - Iron Ore Co. of Canada, Quebec

The sample used was a beneficiated ore from the Wabush mine which contained 64.4 percent iron (our analysis). A fraction screened to -230/+400 mesh was used for leaching tests under standard conditions except that both HCl and H<sub>2</sub>SO<sub>4</sub> were used. Results are shown in Figure 11, lines 20 and 20 A. The material is not reactive, and in 3 hours only 7 - 10 percent was dissolved.

These results are consistent with previous work on the reactions of acid with hematite. Pryor and Evans (1949) found that at 25°C only concentrated hydrofluoric or hydrochloric acid could readily attack hematite. Dilute acids at equivalent strengths all behaved very similarly, and rates were slow and decreased with time. Azuma and Kamentani (1964) obtained very similar results e.g. 10 percent conversion in 1 N H<sub>2</sub>SO<sub>4</sub> after 10 hours at 55°C independent of rate or the kind of acid used. Both the above workers showed that the inertness of the hematite was due to its particular lattice structure. Higher rates are obtained if defects are present (e.g. the higher initial rates observed) or if the lattice is altered by some means such as heat treatment. As a matter of interest, a standard leaching test was carried out on ferric hydroxide prepared in the laboratory (this compound is occasionally available in minor amounts as a commercial waste product.) Results are given in Figure 12, line 21, and show rapid and complete dissolution in dilute acid.

Other materials were obtained, some of which were tested, but either the available quantity or iron content was too small or results were not promising, (usually the former) and so they are not listed here. A summary of the results just given is compiled in Tables IV and V for easier reference.

One source of waste acid, already listed in Table II, was tested in the laboratory. This waste acid, produced by Canadian Titanium Pigments Ltd. at Varennes, Quebec, is approximately 5.9 N and contains about 2 percent by weight iron as ferrous sulphate. Leaching tests were carried out using this acid in both concentrated form and at the standard 1.4 N strength. Our results indicate that it is interchangeable with ordinary sulfuric acid of the same strength. According to the producer the total heavy metal impurities (Cr, V, Cu, Ni, Pb, Mn) are less than about 0.1 percent.

### Discussion of Results

Figure 6 indicates that the estimated amount of soluble iron required in Ontario before 1980 is about 15000 tons/year, and for the region within 100 miles of Toronto, about 10000 tons/year. Whether this is produced as a ferrous or ferric salt, it would be convenient to use only two

Table IV

Materials Yielding Ferrous Salts

(Excluding Ferrous Sulphate and Pickle Liquors)

<u>Company</u>	<u>Location</u>	<u>Material</u>	<u>Production</u>	<u>Average Iron Analysis</u>	
1. Burlington Steel	Hamilton	Mill Scale	3000 Tons/year	72%	
2. Burlington Steel	Hamilton	Electric Furnace Slag	22500 Tons/year	9.7%	Fe
				6.0%	Mn
3. Steel Co. of Canada	Hamilton	Mill Scale	Very large	72-80%	Fe
4. Dominion Foundries and Steel	Hamilton	Fine Mill Scale	7200 Tons/year	74.0%	Fe
5. Ford Motor Company	Windsor	Foundry Dust Scrubber Sludge	4100 Tons/year	12.3%	Fe
				49.0%	SiO <sub>2</sub>
6. Non-ferrous metal Producer	Toronto	Reverbatory Furnace Slag	810 Tons/year	31.1%	Fe
7. Non-ferrous metal Producer	Toronto	Reverbatory Furnace Matte	1000 Tons/year	46.6%	Fe
				5%	Pb
				25%	S, SO <sub>4</sub>
8. Metropolitan Toronto	Toronto	Waste Cans and Metal (proposed process - not yet in production)	25000 Tons/year	95%+	Fe
9. Iron Ore Co. of Canada	Sept. Iles, Québec	Sponge Iron	Laboratory only	80-90%	Fe
10. Steel Co. of Canada	Hamilton	Sponge Iron	Pilot plant only	80-90%	Fe

N.B. All production rates and analyses are values supplied by producers. In some cases, not all iron is acid soluble.

Table V

Ferric Materials

	<u>Company</u>	<u>Location</u>	<u>Material</u>	<u>Production</u> *	<u>Average Iron</u> *	
					<u>Analysis</u>	
11.	Burlington Steel	Hamilton	E. F. Fume	800 Tons/year	24.8%	Fe
					9.4%	Zn
					4.4%	Al
12.	Dofasco (Dominion Foundries and Steel Co.)	Hamilton	Blast Furnace Dust from wet scrubber	43800 Tons/year	44.7%	Fe
					14.8%	C
13.	Dofasco Limited	Hamilton	Basic Oxygen Furnace Fume from wet scrubber	43800 Tons/year	55.2%	Fe
					3.9%	Zn
14.	Dofasco Limited	Hamilton	Ferric oxide from pickle liquor regeneration	7300 Tons/year	69.0%	Fe
15.	Steel Co. of Canada	Hamilton	Ferric oxide from pickle liquor regeneration	11000 Tons/year	69.0%	Fe
16.	Steel Co. of Canada	Hamilton	Open Hearth Furnace Dry Dust from Precipitator	75000 Tons/year	63.9%	Fe
					2.3%	Zn
					.45%	Pb
17.	Steel Co. of Canada	Hamilton	Basic Oxygen Furnace Dry Dust from Precipitator	75000 Tons/year	52.4%	Fe
					3.3%	Zn
					1.3%	Pb
18.	Metro Toronto Water Pollution Control	Toronto	Incinerator Ash from Ashbridges Bay Incinerator	21900 Tons/year (estimated)	3-5%	Fe
					2-3%	Zn
					0.5%	Pb
19.	Aluminium Co. of Canada	Arvida, Québec	Red Mud from Bayer Alumina Process	10 <sup>6</sup> Tons/year	10.0%-	
					12%	Fe
20.	Iron Ore Co. of Canada	Sept Iles, Quebec	Hematite Ore	Very large	64.4%	Fe

\* N.B. All production rates and analyses are values supplied by producers. In some cases, not all iron is acid soluble.

or three sources of supply which are reasonably reliable as to quantity and quality. No by-product material tested was ideal; all had some drawback causing varying degrees of concern.

Mill scale is probably one of the better raw materials, being free of major impurities, and yielding a mixture of ferrous and ferric salts (possibly 50 - 60 percent ferrous). However, some mill scale may require grinding before dissolution, and much of it is oily (particularly the fine grade) and may require preliminary washing. Nearly enough waste mill scale is produced from two sources in Hamilton to supply Toronto area needs for soluble iron.

If a source of sponge iron becomes available in Ontario or Quebec this should be considered as a source of ferrous iron because of its rapid rate of dissolution in dilute acids. In the Windsor area, the foundry waste could supply about one half the probable iron requirements of this region, and this material also is very readily dissolved.

If ferric salts are desired, dust or sludge from steel furnaces (either the open hearth or basic oxygen furnaces) should be considered. These dusts dissolve readily to give ferric salts, and ample amounts are available. However, they also contain significant amounts of zinc and often lead as well. These metals will appear with the iron in the final sludge from a treatment plant, and may affect the choice of method of sludge disposal. Insofar as phosphorus removal is concerned, or their effect on the biological processes in the treatment plant, little effect is expected or has been found in preliminary tests. Metals added with pickle liquors tend to accumulate in the sludges (Fowlie and Shannon, 1973).

Considerable quantities of crystalline ferrous sulphate or of pickle liquor are also available in Ontario. Within about a 100 mile radius of Toronto, possibly 1800 tons/year of soluble iron are available in either crystal or solution form from about twelve producers. This material should be used if at all possible for it represents a very cheap source of iron, available for shipping cost, or shipping cost plus about \$40 per ton of iron, at the most. It would require a heated dissolving or storage tank, depending on whether crystalline ferrous sulphate or pickle liquor was being used, but this would be very inexpensive. Since 1 mgd of capacity would require 20 - 30 tons/year of soluble iron, several producers can

supply sufficient soluble iron for local treatment plant needs. Inasmuch as most of the solid ferrous sulphate or the pickle liquors presently represent a considerable disposal problem, there are very strong reasons for employing this material in local plants for phosphorus removal. An estimate of the cost of using a crystal or a liquor is given in the section on "Costs".

Metro Toronto will shortly produce a very large tonnage of metal waste, largely tin cans, by magnetic separation from solid wastes. This material cannot be recycled to the steel industry unless it is first de-tinned. However, it could be used "as is" to produce iron salts. There seems to be no information on the effect of soluble tin as an impurity in treating plants, although the tin compounds would appear in the sludge. Other problems also exist with the use of cans, since they are not cleaned, or enamels or resins removed except partially in the shredding operation. These unknown factors make it difficult to predict the value of tin cans as a possible source of soluble iron. However, the amount of metal available suggests that their use should be investigated when representative samples are available.

## ESTIMATE OF COST OF PRODUCTION FOR IRON SULPHATES

### Introduction

An analysis has been carried out to determine a representative value for cost of production of iron sulphates from waste materials. No attempt has been made to carry out profitability or return on investment studies, nor has effort been made to optimize the particular process designs used in arriving at costs. Initial cost studies showed that the cost of production is not particularly sensitive to processing alternatives, and hence, the production cost is not very dependent on the particular plant design. Profitability studies can be made from the cost data given in this section, together with the market flow predicted by Figure 5 or Figure 6. When selling costs, and a selling price are established, cash flows and return on investment may be computed according to any scheme desired.

In the cost of production estimates made in this study, the general method used was that suggested by Agarawal et al, (1973). However, capital cost estimates followed the procedures suggested by Peters and Timmerhaus (1968) for preliminary studies. Actual cost data were obtained from this source, and from Jelen (1970), although for major cost items actual quotations from suppliers were used when possible.

All cost estimates are based on manufacture in the Toronto-Hamilton area. An estimate is given of the cost of treating sewage plant influent with iron salt solutions for phosphorus removal, based on a reasonable selling price and average transportation costs to the treatment plant.

### Process Examples

Four example cases were studied in order to evaluate the effects of various factors on the cost of production. Since preliminary studies showed that capital recovery was a minor factor, and the optimum process was not sensitive to first cost, it appeared likely that minimum investment would be favoured. Therefore, in all cases a batch process was assumed, and rather long cycle times were employed ( 6 - 8 hours ), although in the large scale examples, two reactors in parallel were used to give longer filtration cycles. The long cycle times allowed a fairly high conversion

to be assumed in the reactor, thus minimizing filtration cost and the need to recycle large amounts of filter cake. Such recycling would lead to larger conversions, and this can be readily allowed for.

All equipment was assumed to be made of inert plastic, or rubber-lined. Raw material inventory and product storage were both assumed to cover five days operation in all cases. As pointed out previously, alternate processing possibilities, storage or inventory criteria, etc. were not evaluated, although many of these cost factors are parameters whose effects are readily apparent. In every case, for capital recovery straight line depreciation was used with a 10 year service life and zero salvage value assumed. Money was assumed to be worth 10 percent in calculating annual capital recovery costs, and for interest on nondepreciable capital items.

Product containing largely ferrous sulphate was assumed to be 6 - 7 percent iron by weight, and if largely ferric sulphate, a 10 - 11 percent solution was taken to be reasonable.

Table VI lists the basic costs and other criteria used for both operating and capital costs. Only the results of one example (Case I) are given in any detail, and only final figures are given for the other cases.

Table VII lists the operating requirements and costs for Case I, while Table VIII gives the capital items and their estimated costs, and the physical plant cost and final depreciable investment cost. Table IX summarizes these cost figures and includes other cost items.

In Table X the principal cost figures for all cases are summarized, together with the resultant final costs of production as \$/ton of soluble iron. These vary from \$206/ton for a small installation serving a 20 mgd treatment plant (basis is 15 ppm Fe dosage), to \$134/ton for a large plant operating with favourable raw materials. Case I is based on the present requirements of the Metro Toronto system, allowing a dosage of 15 ppm of iron, and shows a cost for a ferric sulphate product of \$165 per ton of soluble iron.

#### Discussion of Production Costs

The major feature of the production cost for plants of 2000 tons/year or more of soluble iron is the high proportion of the cost of production represented by the two basic raw materials, iron and acid. For large plants, these items will be 75%-80% of the production cost, and for small plants



Table VI

Study Criteria

Plant Factors

a. General

Operation: 330 days/year, 24 hours/day (Cases I, II and III)  
Location: Toronto

b. Specific

Case I	Capacity: 7610 tons/year soluble iron Iron Source: Open Hearth Furnace Fume 64 percent Fe (assumed all ferric) 2.4 percent Zn 0.5 percent Pb 1 percent alkalinity as CaO 85 percent overall conversion Product 10 percent iron
Case II	Capacity: 10000 tons/year soluble iron Iron Source: Mill Scale 72 percent Fe (50 percent Fe <sup>2+</sup> , 22 percent Fe <sup>3+</sup> ) 85 percent overall conversion Product 7 percent iron
Case III	Capacity: 10000 tons/year soluble iron Iron Source: Basic Oxygen Furnace Dust 55 percent Fe 3.4 percent Zn 6 percent CaO 66 percent overall conversion of iron Product 10 percent iron
Case IV	Capacity: 550 tons/year soluble iron Iron Source: Mill Scale (as above) 90 percent overall conversion Product 6 percent iron Operation 260 days/year, 8 hours/day

### Operating Cost Factors (at plant site)

1.	Sulphuric acid, 93 percent, tank cars	\$34/ton of 100 percent acid
2.	Mill Scale	\$14/ton of dry solids
	Basic Oxygen Furnace Waste	\$16/ton of dry solids
	Open Hearth Furnace Waste	\$16/ton of dry solids
	Utilities	.
3.	Process Water	20¢/1000 gals.
4.	Power	1¢/KW hr.
	Labour	
5.	Operating Labour	\$4/man-hour
6.	Supervision	25 percent of oper. labour
7.	Benefits and Services	20 percent of (oper. labour + sup.)
8.	Laboratory, General Overhead	40 percent of (5) +(6) +(7)
9.	Maintenance	6 percent/year of physical plant cost
10.	Waste Solids Disposal	\$6/dry ton

### Capital Cost Factors

1.	Equipment purchase and delivery cost	
2.	Installation and Erection	47 percent of purchase cost
	Instrumentation	18 percent of purchase cost
	Piping	66 percent of purchase cost
	Electrical	11 percent of purchase cost
	Building and Site	28 percent of purchase cost
	Services	<u>6</u> percent of purchase cost
		176 percent

Physical plant cost = (purchase cost) 2.76

3.	Engineering	33 percent of purchase cost
	Construction Expenses	41 percent of purchase cost
	Total plant cost = (purchase cost)	3.50
4.	Contactor's Fee	18 percent of purchase cost
	Contingencies	35 percent of purchase cost

Depreciable Capital Investment = (purchase cost) 4.03

### 5. Working Capital

Inventory of acid (5 days), iron source (5 days) and 5 days production  
One month's operating expenses

Table VII

Case I

Operating Requirements and Costs, \$/year

	<u>\$/year</u>
1. Sulphuric Acid, 69.6 tons/day 100 per cent acid (74.84 tons/day 93 per cent acid)	780910
2. Open Hearth Dust, 42.4 tons/day (dry basis)	223910
3. Process Water, 25,000 gals/day	1650
4. Power, 50HP	2950
5. Operating Labour, 4 men/day	46720
6. Supervision, 25 per cent	8760
7. Benefits and Services, 20 per cent of (5) + (6)	8760
8. Laboratory, General over head, 40 per cent of (5) + (6) + (7)	21020
9. Maintenance, 6 per cent of \$427,800	25670
10. Waste Solids Disposal, 6.36 ton/day	<u>12590</u>
Total annual operating expenses	<u>1132940</u>

Table VIII

Case I

Capital Cost Estimates

<u>Purchased Equipment</u>	\$
Acid Storage, 40000 gals.	16000
Reactors, 2 at 6000 gals. each, with 15 HP agitators	28000
Pumps - Acid Proof with motors, 4 required	4000
Filter, Rotary Pressure, 50 sq. ft. filtering surface	30000
Product Storage, 2 tanks at 100000 gals. each	54000
Payloader, 27 cu. ft.	14000
Insulation of Product Storage and Lines	4000
Solids Handling Aids	<u>5000</u>
Total purchase cost	<u>155000</u>
<u>Physical Plant Cost</u>	
Installation and Erection	72850
Instrumentation	27900
Piping	102300
Electrical	17050
Building and Site	43400
Site Services	<u>9300</u>
Total physical plant	<u>427800</u>
<u>Total Plant Cost</u>	
Engineering	51150
Construction Expenses	<u>63550</u>
Total plant cost	<u>542500</u>
<u>Total Depreciable Investment</u>	
Contractor's Fee	27900
Contingencies	<u>54250</u>
Depreciable Investment	<u>624650</u>
<u>Working Capital</u>	
Inventory, sulphuric acid and iron source, 5 days supply	15220
One month's operating expenses	<u>94410</u>
	<u>109630</u>

50%-60%. Clearly, reduction in acid costs, and to a lesser extent iron costs, will result in the largest savings.

As a consequence of the importance of acid costs, the cost of production of a largely ferrous product is significantly less than that of a ferric product, since up to 50% less acid may be required.

Investment costs for plants of different capacities using the same raw materials can be predicted quite closely from the "six-tenths" rule, that is, the ratio of costs can be found by taking the ratio of capacities to the 0.6 power (for example for Cases II (a) and IV (b) this power is 0.64).

The higher production cost for Case III compared to Case I (both producing mainly a ferric sulphate product) is due to a combination of lower conversion assumed for the basic oxygen furnace fume, and the much higher lime content of the B.O.F. fume, which consumes acid. If an 80% conversion of iron from the B.O.F. dust can be attained (e.g. by recycling of filtered solids), then the production cost drops from \$195 to \$186 per ton of soluble iron.

The above results focus attention on the possibility of use of a ferrous product rather than ferric. Two potential problems may exist with the use of ferrous salts. First, the system must have sufficient aeration capacity to rapidly carry out the oxidation of the ferrous hydroxide to ferric hydroxide. Secondly, in cold weather (below freezing) crystallization of ferrous sulphate heptahydrate can occur with possible operating problems. If a ferrous sulphate solution is stored hot in an insulated tank, there is no danger of freezing before use. For example, a 100000 gallon tank with three inches of insulation holding ferrous sulphate at 200°F will lose less than 2° per day if the outside temperature is -15°F. If filled at Christmas, it would still be warm in April. The real problem lies in transfer lines, which should be well insulated, or even heated, and metering equipment which should preferably be located indoors.

Finally, in any plant producing iron salts, attention must be paid to the heat balance. The heat of reaction is high, and no auxiliary heating should be necessary. In fact, some minor degree of cooling of the reactor may be required to hold the temperature below about 200°F.

Table IX

Case I

Cost Summary

<u>Investment Required</u>	\$
Depreciable Investment	625000
Working Capital	109630
<u>Production Cost, \$/year</u>	
Operating Expenses	1132940
Capital Recovery, (10 years @ 10%, straight line)	101720
Interest on working capital @ 10%	10960
Property Taxes	12500
Insurance	<u>630</u>
Total annual cost at design capacity,	
\$/year	<u>1258750</u>
Production 7610 tons/year	
Cost of Production = \$165.41/ton of soluble iron	

Note: If an overall 95% iron recovery was assumed at the same production rate (by recycle of filter cake to reactors), cost of production is about \$161.27/ton of soluble iron.

Table X

Summary of Production Cost Estimates

<u>Case No.</u>	<u>Operating Criteria</u>	<u>Depreciable Investment</u>	<u>Working Capital</u>	<u>Annual Operating Costs</u>	<u>Production Cost \$/ton Fe</u>
I	Open Hearth Furnace Dust 330 days/year, 24 hours/day 7610 tons Fe/year Product 10% Fe	625000	109600	1258800	\$165.40
II	(a) Mill Scale, 22% Ferric, 50% Ferrous, 330 days/year, 24 hours/day, 10000 tons Fe/year Product 7% Fe	810400	113400	1179800	\$134.00
	(b) Mill Scale, Fe <sub>3</sub> O <sub>4</sub> Capacity as for II(a) Product 6% Fe	798000	125200	1313500	\$147.30
III	Basic Oxygen Furnace Fume 330 days/year, 24 hours/day 10000 tons Fe/year Product 10% Fe	741500	169300	1801500	\$195.47
IV	(a) Mill Scale as in II (a) 260 days/year, 8 hours/day 550 tons Fe/year Product 6% Fe	175000	7800	80170	\$206.60
	(b) Mill Scale as above 330 days/year, 24 hours/day 2090 tons Fe/year Product 6% Fe	296000	28500	291200	\$167.10

## COST OF IRON SALTS FOR PHOSPHORUS REMOVAL

To determine a possible cost of ferrous or ferric sulphate solution to a treatment plant it is necessary to add freight and selling expenses, and a reasonable return on investment. Return on investment can be calculated in many ways, and the method used depends partly on the circumstances. For a large plant operated for some time initially at partial capacity, a discounted cash flow method may be used. For plants built to serve an immediate market (for example, a small unit to serve one locality, or for a single large metropolitan market), the plant will operate at nearly design capacity from the beginning. In this case, a simple return on investment  $\left[ = \frac{(\text{sales} - \text{cost of production} - \text{cost of sales})}{\text{investment}} \right]$  may be an adequate indicator of a fair selling price at the production plant site. In evaluating a reasonable return on investment, (before income taxes) it must be remembered that recovery of capital or interest on working capital at a rate of return of 10% is already built into the cost of production figure.

Freight costs on the basis of transport in stainless steel tank truck lots can be approximately estimated for distances up to 300 miles from the formula given below, deduced from quotations received.

$$\text{Freight cost, \$/ton of liquid} = \$4.40 + 0.048 M$$

Where M = miles transported.

Selling and technical service costs can be assumed to be 4% of the selling price.

On this basis, for a ferric sulphate material produced by a plant in Toronto of the capacity given as Case I, a fair selling price F.O.B. the Toronto plant would be about \$197/ton of soluble iron. This figure would allow a simple rate of return of about 30% before taxes. On a discounted cash flow basis this selling price represents a rate of return before taxes which is also about 30%.

At this selling price, the cost of this product at 10% soluble iron by weight (15 lbs. per gallon) for a plant 100 miles from the supplier would be \$289 per ton of soluble iron.



## COMPARISON OF TREATMENT COSTS

Because a range of dosage levels is possible, a comparison of costs of chemicals for phosphorus removal is difficult to make explicitly. However it can be assumed that some average dosage will be used as a basis for cost comparisons.

For the Toronto area, the selling price for ferrous or ferric sulphate, from almost any source material, should be about \$200 or less per ton of soluble iron. At dosage rates from 10 ppm - 20 ppm, this represents a chemicals cost of \$10 to \$20 per million gallons treated. This cost may be compared to alum, which in the Toronto area has a selling price of about \$58/ton of dry alum. For dosage rates ranging from 70 to 140 ppm, chemicals costs would be \$20.30 to \$40.60 per million gallons. Ferric chloride is presently being purchased in Toronto at \$106.80 per ton of  $\text{FeCl}_3$ , or \$310 per ton of soluble iron. Using this chemical, treating costs of \$15.50 to \$31.00 per million gallons can be expected.

For treatment plants not situated in the vicinity of a producer of iron salts, it would appear that ferric sulphate solutions 10% or more by weight of soluble iron can readily be shipped up to 100 miles by tank truck and still have the possibility of significant savings over other treatment chemicals. If ferrous sulphate solutions of 6-7% soluble iron are being shipped, then this conclusion is still true, because ferrous sulphate solutions should sell for less, and this selling price reduction could be enough to largely offset the extra freight charges. For example, a ferrous sulphate solution produced on a fairly large scale at 6-7% concentration might sell in Toronto for \$175-\$185 per ton of soluble iron. Freight costs for a 100 mile haul would be about \$140/ton, giving final cost of perhaps \$320 per ton. However, freight charges of this magnitude mean that ferrous sulphate solutions are best used close to the source of manufacture. These conclusions do not apply to the use of crystalline ferrous sulphate, and its possible use on site by smaller treatment plants should not be overlooked. This salt can probably be purchased bagged for about \$100 per ton of soluble iron, and even if shipped 100 miles it would still cost at the treatment plant only about \$130 per ton of soluble iron. At this level, for a small plant, e.g., 1 to 10 mgd, the cost of heating and insulating a dissolving tank or putting the dissolving and metering equipment under cover is a small fraction

of the possible savings, which could range from \$5000-\$30000 per year. As long as a supply of crystalline ferrous sulphate is available as a waste product (see Table II) at low prices, very serious consideration should be given to its use in smaller plants. Again, adequate aeration capacity is assumed to be available to oxidize the ferrous iron to ferric iron.

It should be pointed out that ferrous chloride  $\text{FeCl}_2$  has a greater solubility than ferrous sulphate, and concentrated solutions have much lower freezing points. If cheap hydrochloric acid, or chlorine, were available, ferrous chloride solution could be a very satisfactory alternative. However, at the present time, hydrochloric acid is two to three times the cost of sulfuric acid.

So far, no mention has been made of impurities in solutions of ferrous or ferric sulphate obtained from waste iron sources. Allowance has been made in cost figures for acid consumption by these soluble impurities, but no penalty or credit apart from this has been allocated for impurity content in the iron salt solutions. These impurities are present mainly in the fumes from steel mill furnaces, slags, or in some pickle liquors derived from alloy pickling. In sulphate solutions, these impurities will be mainly zinc and manganese, with lesser amounts of copper, chromium, lead and other heavy metals. Many of these impurities are also effective in phosphorus removal, and most of them will appear in the sludge. The tolerance levels for many of these extraneous metals have not been clearly established, but present knowledge suggests that in the amounts likely to be added in treating chemicals, their effects on treatment plant performance can be ignored. It is not so certain that this is true for the sludge, since metal concentrations tend to be much higher in the solids, and may affect the value of the sludge for agricultural purposes, for example.

On the other hand, ferrous and ferric salts can be made from relatively "clean" iron sources, for example, mill scale, scrap, sponge iron, some iron ores, etc.. The most readily available and least contaminated waste sources of iron tend to give a larger proportion of ferrous ion, and ferrous sulphate solutions are likely to have the highest purities.

## SUMMARY

1. In neutral oxidizing solutions, ferrous ion very rapidly oxidizes to ferric ion. In acid solution, this oxidation rate is very slow. Therefore, either ferrous or ferric ion can be added to remove phosphorus ion, since in neutral waste waters the ion will rapidly be converted to the ferric form. Similarly, it is not practical to attempt to oxidize acid solutions of ferrous salts to the ferric form prior to addition to the waste water unless powerful oxidizing agents are used.
2. Market estimates of the usage of iron salts for phosphorus removal in Ontario have been made. On the basis of the assumption that about 75% of the market demand for treating chemicals will be met by iron salts, and assuming an average dosage rate of 13.5 ppm, about 15000 tons/year of soluble iron will be needed in Ontario by 1980. In the Toronto area (up to 100 mile radius), about 10000 tons/year of soluble iron will be consumed.
3. The potential market is large enough to justify a manufacturing operation, since the only iron salt now produced in significant quantities in Ontario and available for phosphorus removal is ferrous sulphate crystal or solution. The present total iron salt production in Ontario available commercially is less than 20% of the probable 1980 demand.
4. Industrial waste products containing iron are produced in Ontario in a quantity exceeding considerably the demand for soluble iron for phosphorus removal. In many cases, these wastes represent disposal problems for their producers, and add to the costs of production. Similarly sulphuric acid is in excess supply, and the disposal of potential production of sulphuric acid is a significant industrial problem in Ontario. Therefore, manufacture of iron sulphate salts from waste iron sources and sulphuric acid would represent a very desirable development for this province.

5. Inasmuch as iron salts are a waste product produced in large amounts in the United States, and represent a serious waste disposal problem for some American manufacturers, importation of iron salts will be preferred by many present and potential suppliers of phosphorus treatment chemicals for the Ontario market. From the viewpoint of the economy of the province in general, use of imported iron salts for this purpose could result in nothing but substantial loss of economic benefits. Since the local (provincial) manufacture of iron salts is likely to result in cost reductions over present prices for phosphorus treatment chemicals, such local manufacture should be required by government agencies, and this is a major recommendation of this study.
6. The amounts and compositions of many iron containing waste products available in Ontario have been tabulated. Materials of potential value as iron sources have been tested for their ease of dissolution in dilute sulphuric acid, and the proportions of ferrous to ferric sulphate produced have been determined. Results of these reactivity tests are given for the waste materials as normally produced. Since, in general, the rate of dissolution is directly proportional to acid strength and to solid surface area present, these dissolution tests can be used to estimate process behaviour under different conditions.
7. Preliminary designs have been carried out for processes to manufacture iron sulfate solutions from sulphuric acid and waste sources of iron. From these designs, cost of production figures and investment requirements have been estimated for a number of plant sizes. Raw materials form 50-60% of the production cost for small plants (up to 2000 tons or iron/year) and 70-80% of the production cost of larger plants (over 7000 tons of iron/year). Of this, the major part is the cost of sulphuric acid. Because of this factor, solutions containing ferrous sulphate are significantly cheaper to manufacture than ferric sulphate solutions.
8. The use of ferrous sulphate solutions is complicated by its lower solubility and freezing point. Ferrous sulphate solutions will need to be stored and used somewhat above 32°F. Costs of using ferrous sulphate solutions are such that the necessary heating and/or insulation of

storage tanks, lines and metering equipment would be a small fraction of the potential savings. The treatment plant also must have some minor excess aeration capacity to supply the increased chemical oxygen demand arising from using ferrous salts. In most treatment plants, this latter aspect is not a problem.

Waste sources of iron which yield mainly ferrous salts are readily available and tend also to contain fewer impurities than do the waste materials yielding mainly ferric salts.

9. The cost of a phosphorus removing chemical per million gallons should be less if locally produced ferrous or ferric sulphate is used than for other chemicals. Treatment costs are estimated at \$10 to \$30 per million gallons depending on dosage and distance from the producing plants. From cost data given, estimates of treatment cost for various localities can be worked out. In nearly every case, the lowest cost for treatment chemicals will result from the use of ferrous or ferric sulphate solution or ferrous sulphate crystal.

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